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DMIC Report 216
May 10, 1965

CORROSION OF MATERIALS BY ETHYLENE GLYCOL-WATER

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CORROSION OF MATERIALS BY ETHYLENE GLYCOL-WATER

by

J. D. Jackson, P. D. Miller, F. W. Fink, and W. K. Boyd

to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus, Ohio 43201

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CORROSION OF MATERIALS BY ETHYLENE GLYCOL-WATER

J. D. Jackson, P. D. Miller, F. W. Fink, and W. K. Boyd*

SUMMARY

Solutions of ethylene glycol are being considered as heat-transfer media for radiators in manned space capsules. Most available corrosion data, however, are based on automotive and diesel engine coolant systems.

In the presence of oxygen, solutions of ethylene glycol at elevated temperatures tend to decompose into glycolic and formic acids. The presence of such decomposition products tends to increase the corrosion rates of most metals in glycol solutions. It is, therefore, recommended that ethylene glycol systems be designed as closed nonaerated systems.

In space applications, the lighter metals such as aluminum, magnesium, beryllium, or titanium would be candidate materials of construction. Of these metals, titanium would be expected to be highly resistant. Corrosion rates of aluminum in uninhibited solutions would be of the order of 1-2 mpy, while magnesium probably would have low corrosion rates only with an inhibitor added. Rates of attack for beryllium would be somewhere between those for aluminum and magnesium.

Heavy metal ions such as copper would be expected to increase attack and cause pitting of aluminum, beryllium, and magnesium unless adequately inhibited. The light metals should not be coupled to dissimilar metals in ethylene glycol solutions.

In uninhibited glycol solutions, the corrosion rates of all metals studied were found to be constant with time or to decrease. When the glycol solution was continuously renewed, the corrosion rate of copper, brass, steel, cast iron, solder, and aluminum was constant. In 40 percent glycol at 160 F, the corrosion rate is about 10-20 mpy for steel and cast iron, and 1-2 mpy for the others. Without solution renewal, the rate of attack on steel and solder was nearly constant; while that for copper, brass, and aluminum decreased to a low value. At a pH of 6-10, all metals evince a nearly constant rate of attack. Above pH 10, the corrosion rate of steel and cast iron decreased rapidly, while brass and copper increased slightly, and aluminum and solder increased rapidly. The corrosion rate of steel decreases as the glycol concentration increases. An increase in temperature causes increased attack on all metals. Aeration or oxygen increases the attack of the metals studied, as does the chloride ion.

Galvanic attack can occur in glycol solutions, increasing the attack of the less resistant of two coupled metals. Steel is the least resistant followed by cast iron, aluminum, solder, brass, and copper. Pitting can sometimes occur on aluminum when coupled to other metals.

No velocity effects were found for a clad aluminum alloy up to a velocity of 3000 ft per minute. Under conditions of heat transfer, the corrosion rate of cast iron increased.

With the addition of suitable inhibitors to glycol solutions, the corrosion rates of most metals can be reduced to a negligible value. Some inhibitors, however, are specific to certain metals and will increase the attack on others. In addition, ions from one metal can increase the corrosion of another even though the two are not in direct contact. Thus, in cooling systems where several different metals are present, a combination of compatible inhibitors is often required for adequate protection.

Among the most common corrosion inhibitors which have found successful use in ethylene glycol solutions are:

(1) Borax, usually with additives

(2) Sodium benzoate-sodium nitrite

(3) Triethanolamine phosphate (TEAP)-sodium mercaptobenzothiazole (MBT).

A number of patented inhibitors, based on borax, are listed.

An inhibitor system used by the U. S. Military consists of 1.8 percent borax and 0.024 percent MBT. In recently revised specifications, sodium phosphate is added to protect aluminum alloys. This inhibitor is 1.7 percent borax, 0.10 percent MBT, and 0.06 percent sodium phosphate.

A common British inhibitor contains 1.5 percent sodium benzoate and 0.1 percent sodium nitrite. The benzoate protects mild steel, aluminum, and solder, but not cast iron. The nitrite inhibits attack on cast iron as well as copper and brass but causes attack of solder. The combination prevents attack of both cast iron and solder, as well as mild steel, copper, and brass. Corrosion on aluminum has been found to increase when the pH rises from 8 to 11. The inhibitor may also cause some deterioration of neoprene rubber.

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Another British inhibitor contains 0.19 percent phosphoric acid, 0.4 percent triethanolamine, and 0.041 percent MBT. TEAP by itself causes corrosion of copper and of aluminum and steel, if copper is in the same system. MBT prevents this attack. Of several metals tested, only nickel seemed adversely affected by this inhibitor system.

Soluble oils have been suggested as inhibitors for glycols but not all perform satisfactorily. Many soluble oils which are excellent metallic corrosion inhibitors have a detrimental effect on rubber.

Chromates may also be adequate inhibitors for glycol systems in the absence of light and when properly maintained. Their use is not recommended, however, without additional investigation.

Various other inhibitors are suggested for specific uses such as potassium sulfide for magnesium.

Corrosion inhibitors become rapidly depleted under conditions of a rusty cooling system, high-speed engine operation, or excessive aeration. Protection of a system may be maintained for a few months to over a year, or 2000 to 20,000 miles, depending on the inhibitor system and the operating conditions. The measurement of pH is not necessarily a good indication of the corrosiveness of the coolant.

INTRODUCTION

Solutions of ethylene glycol and water have, for a long time, been important in cooling systems for land vehicles employed by the Army and amphibious vehicles employed by the Navy. Such solutions are now being considered as heat-transfer media for temperature-control systems in manned space capsules. In the latter, it is desirable to use light metals such as magnesium, beryllium, titanium, and aluminum. Consequently, knowledge of the compatibility of these metals with glycol-water mixtures is important not only to this application but to other aerospace or military applications where thermally efficient, light-weight components are required in heat-transfer systems that operate in the range of -50 F to 250 F.

At the outset of this task, it was recognized that comprehensive corrosion data for ethylene glycol solutions are not available in the trade journals or literature. This derives from the fact that the information concerning corrosion inhibitors and other additives which have been developed for commercial antifreezes is largely proprietary. Consequently, to obtain further information on the effects of these ingredients on the corrosion aspects of glycol-water mixtures, a fairly comprehensive patent search was included as a part of this survey. The resulting summary presents what DMIC believes to be an accurate and fairly comprehensive picture on the corrosion behavior of various metals and alloys in glycol-water mixtures, both with and without inhibitors.

PHYSICAL AND CHEMICAL PROPERTIES

Diethylene glycol or glycol is a colorless liquid which melts at 3.9 F and boils at 387.3 F at atmospheric pressure. Its formula is $CH_2OH \cdot CH_2OH$ and molecular weight is 62.07. Its density at 66 F is 1.113 g/cc and its heat-transfer coefficient is 1.86 Btu/hr sq ft F/in. at 32 F. In a concentration to give a freezing point of -20 F, its expansion from 40 to 180 F is 4.6 percent compared to 5.5 and 6.75 for methanol and ethanol solutions.(1)* Water would expand 3.0 percent.

The freezing points, boiling points, and densities of Prestone** antifreeze (97 percent glycol) are shown in Table 1. A comparison with other antifreeze solutions is shown in Figures 1, 2, and 3.

Decomposition of Glycol

Under conditions of high temperature and in the presence of oxygen, ethylene glycol tends to decompose. Collins, et al,(4) state that the acids which can be formed in a glycol cooling system are as follows: carbonic, sulfurous, or sulfuric

TABLE 1. FREEZING AND BOILING POINTS AND DENSITY OF PRESTONE COMMERCIAL ANTIFREEZE(2,3)

Wt%	Vol%	Density,(2) 60 F, g/cc	Freezing Point, F(2)	Boiling Point, F(3)
10	9.2	1.013	25.6	213
15	13.8	1.019	22.0	214
20	18.3	1.026	17.8	215
25	23.0	1.033	12.8	216
30	28.0	1.040	6.8	217
40	37.8	1.053	-8.2	219
50	47.8	1.067	-28.8	223
60	58.1	1.079	-56.7	--
100	100	1.113	3.9	387.3

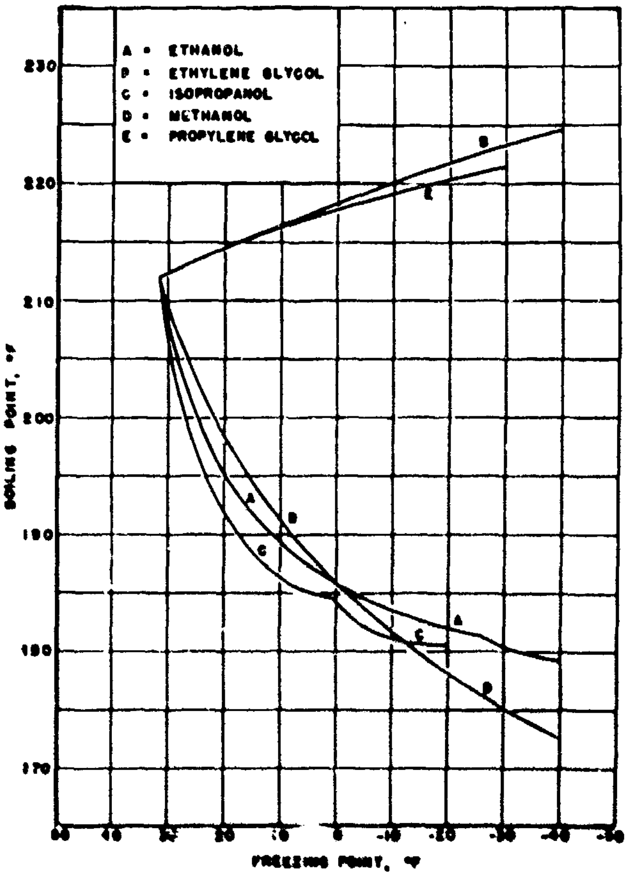

FIGURE 1. VARIATION OF BOILING POINTS OF ANTIFREEZE SOLUTIONS WITH FREEZING-POINT PROTECTION(3)

The boiling-point temperatures on this chart decrease nearly 2 F for each 1000-feet elevation above sea level.

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*References are given on page 14.

**Commercial Antifreeze, Trade Mark of Union Carbide Corporation.

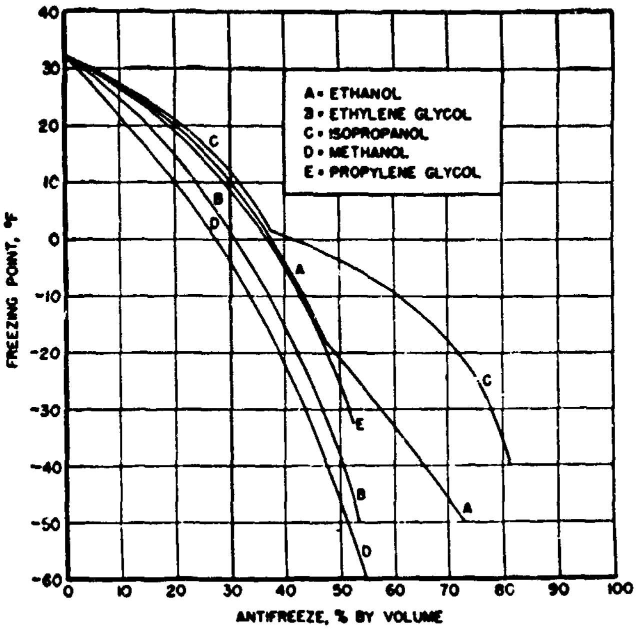

FIGURE 2. RELATION OF CONCENTRATION TO FREEZING POINT FOR ANTIFREEZE SOLUTIONS(3)

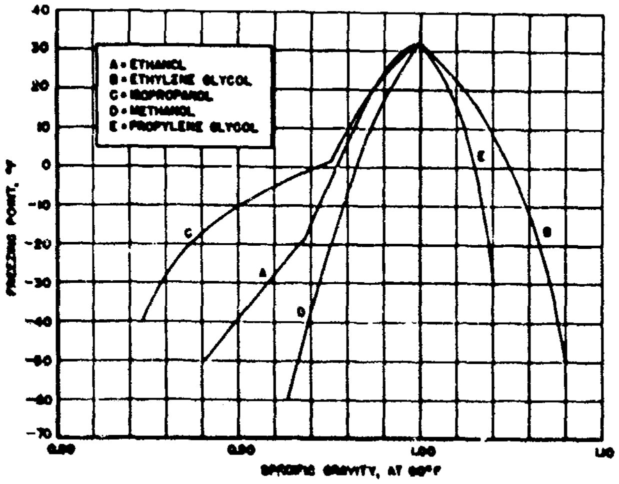

FIGURE 3. RELATION OF SPECIFIC GRAVITY TO FREEZING POINT FOR ANTIFREEZE SOLUTIONS(3)

from combustion gases, or glycolic, glyoxylic, oxalic, or formic acid from the oxidation of the glycol. Analysis, however, of many used antifreeze solutions has not indicated the presence of acids from combustion products. Neither have glyoxylic or oxalic acids been detected. On the other hand, glycolic and formic acids have been detected and measured.(4)

Lloyd, et al,(5) have shown quantitatively the amount of free acid decomposition products as a function of temperature and oxygen concentration. See Tables 2 and 3. The data include free acids only (excluding esterofied acids), and the total acid formation is considerably greater.

TABLE 2. EFFECT OF AERATION RATE ON FREE ACID FORMATION IN DIETHYLENE GLYCOL(a)(5)

Gas	Oxygen Rate, ml/min/100 ml glycol	Free Acid, meq/liter
N_2	0.0	0.0
CO_2	0.0	2.0(b)
H_2S and O_2	1.0	13
O_2	5.0	27
Air	19.0	45

(a) 48-hr reflux tests 95% glycol-5% water at 295 F.

(b) Probably H_2CO_3.

TABLE 3. EFFECT OF TEMPERATURE ON FREE ACID FORMATION IN DIETHYLENE GLYCOL(a)(5)

Aeration Rate, std cu ft/day	Temp, F	Free Acid, meq/liter
1.7	392	172
1.7	295	145
1.8	241	83
1.7	203	45
1.9	176	33
1.5	81	0.4

(a) 24-hr aeration tests, undiluted glycol.

In terms of corrosion, this means that a closed nonaerated system is preferred. There should be less attack on the metals in a closed system. In automobiles, mechanical defects such as loose or leaky head gaskets, air leakage at the suction or input to water pumps, or loose hose connections should be prevented. Local hot spots, operation of the coolant at consistently high temperatures, and large amounts of copper or copper alloys in the system are also suggested as promoting oxidation of glycols in service.(4)

CORROSION BY ETHYLENE GLYCOL

The published corrosion data for ethylene glycol are generally concerned with engine-coolant experience. Factors which may influence corrosion are:(6)

(1) Coolant flow
(2) Aeration
(3) Operating temperatures
(4) Water composition variables
(5) Corrosion by-products
(6) Antifreeze characteristics
(7) Couples of dissimilar metals
(8) Exhaust gas leakage into coolant
(9) Metal hot spots
(10) Metal stresses
(11) Operating conditions.

The most common materials of construction exposed in glycol are those found in an engine cooling system, i.e., cast iron, mild steel, copper, brasses (70Cu-30Zn, 85Cu-15Zn), solder (70Pb-30Sn), and aluminum [usually unalloyed, but sometimes Type 3003 (1.2Mn, 0.70Fe, 0.60Si) or silicon cast aluminum]. Data on other metals and alloys are presented in the tables where available.

The test procedures used to obtain the corrosion data for uninhibited ethylene glycol and several inhibitor systems for ethylene glycol are described in the Appendix.

Uninhibited Ethylene Glycol

The factors which affect corrosion of metals in ethylene glycol can best be described by data from the uninhibited and pure system. The factors are discussed briefly in the following sections. The corrosion data are presented in Table 4, which has been divided into sections for easy reference.

Time Dependence

No data are presented in Table 4 for the effect of time, this factor can be summarized as follows:

The corrosion rates of representative metals in ethylene glycol were found to be constant with time or to decrease with time.(7) When the glycol solution was continuously renewed the corrosion rate of copper, brass, steel, cast iron, solder, and aluminum was constant. With nonrenewal of solution, results are erratic and the solution became more acid. Steel maintained a nearly constant rate, however, since its corrosion is nearly constant over the pH range of 4 to 11. Solder also showed about the same rate in unrenewed as in renewed solution. Copper, brass, and aluminum had a high initial corrosion rate which dropped to a negligible rate without solution renewal. With copper and brass, the difference in corrosion rate was found to be dependent on the copper ion concentration.

When copper and aluminum were in the same solution, the copper tended to precipitate out on the aluminum, causing increased attack of the aluminum.(17) See also, Galvanic Corrosion.

Effect of pH

The effect of pH was shown by using high-purity ethylene glycol and adjusting the pH with oxalic acid and sodium hydroxide. Of the metals tested, all showed a nearly constant rate of attack between pH 6 and 10.(7) Below pH 6 the rate of attack increased rapidly for all metals tested. Above pH 10, the corrosion rate of steel and cast iron decreased rapidly, while brass and copper increased slightly. Aluminum and solder are attacked rapidly at the higher pH. (See Sections A and B, Table 4.)

Effect of Concentration

No consistent change in corrosion rate was noted for any metals except steel with increasing glycol concentration.(7) (See Section C, Table 4.) Contrary to popular opinion, the corrosion rate of steel is 20 times less with 60 percent glycol than with water at 160 F.

Effect of Temperature

In general, an increase in temperature caused an increase in corrosion rates of the metals studied.(1,7,9,10) (See Sections D, E, and F, Table 4.) The greatest increase, however, was in the corrosion rate of steel, which went from 0.5 mil/year at 80 F to 39 mil/year at 220 F.(7) It is reported that ethylene glycol solutions at normal temperatures produce negligible attack on magnesium or magnesium coupled to steel. At 240 F, the normal corrosion rate increases to some extent and galvanic corrosion will occur unless the solutions are inhibited.(12)

Effect of Aeration

Aeration had a pronounced effect on the metals studied with constant solution renewal except for steel at pH 4 and aluminum at all pH levels.(7) The corrosion rates were much reduced in the absence of oxygen. The oxide film on aluminum was found to be protective in the absence of oxygen even when chloride ions were present to 20,000 ppm (compare Sections A and B, Table 4).

As mentioned previously,(5) ethylene glycol decomposes to acidic compounds in the presence of oxygen. This tends to increase the rate of attack on most metals.

Effect of Chloride Ion

The addition of chloride ion to ethylene glycol solutions tends to increase the corrosion. In solutions containing up to 200 ppm chloride, the most severe increased attack occurred on steel and cast iron.(6,7) The corrosion of solder also increased somewhat.(7) In solutions containing 2 g/l NaCl and 1 g/l Na_2SO_4, copper and brass, as well as steel and cast iron, showed an excessive increase in corrosion.(6) Magnesium also showed a high rate of attack in chloride-containing water(12) (compare Sections G and I, Table 4, to appropriate parts of Sections A, C, or D).

Galvanic Corrosion

When dissimilar metals are in contact, corrosion of the less resistant metal is increased, thus further protecting the more resistant member of the couple. In general, this is also true with ethylene glycol solutions at room temperature.(6) The data show that steel is least resistant, followed by cast iron, aluminum, solder, brass,

TABLE 4. UNINHIBITED ETHYLENE GLYCOL CORROSION

Section	Glycol, %	Temp, F	pH	Aeration	Reference	Cu	Brass	Steel	Cast Iron	Solder	Al	Sn	Cd	Pb	SS	Mg	Ni	Ag	Ti	Zn	Other
						Corrosion, mils per year															
A	40	160	4	Yes	7	12	12	17	29	2.3	11										
	40	160	7	Yes	7	1.5	1.7	12	20	0.4	0.5										
	40	160	9	Yes	7			12		0.1	1.5										
	40	160	11	Yes	7	2.7	3.0	0.1	14	40	57										
B	40	160	4	No	7	Gain	Nil	19		1.0	1.3										
	40	160	7	No	7	Gain	Nil	2.5		0.9	1.0										
	40	160	11	No	7	Nil	Gain	0.1		1.0	120										
C	0	160	7	Yes	7,8	Nil	Nil	19-34	40	0.3	2.2										Al and 53Al-8Cu-4Si-2Zn casting
	20	160	7	Yes	7	1.5	1.7	19		2.2	1.4										
	40	160	7	Yes	7	1.5	1.8	12		0.4	0.8										
	60	160	7	Yes	7	0.9	1.3	1		2.7	0.3										
	33	170		Yes	1	4	3	11		0.9	2										
D	40	-10	7	Yes	7	Gain	Gain	0.04	0.2	0.04	0.03										Al and 83Al-8Cu-4Si-2Zn casting
	40	80	7	Yes	7	Nil		0.5		0.3	Nil										
	40	120	7	Yes	7	0.2		8		0.4	Nil										
	40	160	7	Yes	7	1.4		12		0.4	1										
	40	220	7	Yes	7	1.7		39		0.1	1										
E	50	-10			9															0.04(a)	
	50	20			9	0.02	0.02			0.07	Nil	Nil	0.3	8	Nil	4.3	Nil	Nil	Nil	0.3(a)	
	50	75			9															0.6(a)	
	50	170		Yes	6,9	2	0.7	84	14	2.4	0.5									8(a)	
	50	212			10				42		8										
	50	284			10				1.9		23										
F	100	75			11	<20	<20	<2	<20(b)		<2			20-50	<20(c)		<20(d)	<2			<2, Au, graphite, Pt or Ta
	100	175			11				<20(b)									<2			
	50	212			11						<2										<2(e) Au, Pt, Ta
	75	95			12											1(f) Note: Mg-6Al-0.2Mn					
	95	261			12											12 Note: Mg-8.5Al-0.5Zn-0.2Mn					
G	0(g)	RT	7		12											>250(f)					
	40(h)	160	7	Yes	7	1.2	0.9	14		2.9	1.4										Al and 83Al-8Cu-4Si-2Zn casting
	50(g)	170	7.5	Yes	6	2.1	0.7	84	14	2.4	<0.5										Type 3003
	50(i)	170	7.5	Yes	6	30	18	85	16	2.1	1.6										
H	50(i)	RT	7.4	No	6	Nil(j)	Nil(f)	1.9(k)	2.1(l)		1.1(l)										
	50(i)	RT	7.4	No	6	Nil(m)	Nil(j)	1.5(m)	0.1(f)		0.7(k)										
	50(i)	RT	7.4	No	6	Nil(n)	Nil(m)	1.3(j)	2.0(k)	0.8(l)	0.1(f)										
	50(i)	RT	7.4	No	6	Nil(f)	Nil(n)	2.0(l)	0.9(j)	0.9(k)	0.2(m)										
	50(i)	RT	7.4	No	6	Nil(k)	0.1(l)			Nil(j)	0.3(n)										
	50	RT	7.5	No	6						5-17(k,l,m,n,p)										
I	30	RT			13	Nil(m)	0.2(o)	0.5	0.5(l,j)	—(o)	0.02(l,m)										
	33(g)	140			14	0.4			2.3			0.06(q)	2.6(r)	1.5(r)	0.002						
	30(g)	176(s)		Yes	13	Nil(m,j)	2.3(n)	9.8	14(l)	2.3(k)	2.5(m,l)										Al and 94Al-1.2Cu-0.9Ni-1 Fe-2.3Si-0.1Mg casting
J	50(g)	180		Yes	15						2(t)										No. 100 with Al-Zn clad
	50(g)	180		Yes	15						4(t)										
	50(g)	180		Yes	15						>24(t)										
	50(g)	180		Yes	15						>80(t)										
K	20	176		Yes	16				220												
	20	176		Yes	16				710(u)												
	20	176		Yes	16				>1400(v)												
	20	176		Yes	16				2200(u,v)												

(a) Galvanized steel.
(b) Silicon iron, all concentrations.
(c) 12Cr, 17Cr, 18-8, Type 316.
(d) Ni-resist, Monel, nickel, Inconel.
(e) All concentrations to 212 F.
(f) Coupled to steel.
(g) Tap water.
(h) 200 ppm chloride in water.
(i) Tap water plus 2 g/l NaCl and 1 g/l Na_2SO_4.
(j) Coupled to aluminum.
(k) Coupled to brass.
(l) Coupled to copper.
(m) Coupled to cast iron.
(n) Coupled to solder.
(o) Solder joint broke after 5 months.
(p) Pitting attack depth of pits in mils in ten months.
(q) On copper.
(r) On steel.
(s) Simulated service, heated 8 hr/day.
(t) 1-1/2"-dia Al-clad disk rotated at the following velocities respectively: static, 2900, 3300 and 4700 ft/min. Note: flow in automobile radiator is 300-400 ft/min.
(u) Heat transfer through specimen ~ 76,000 Btu/hr sq ft.
(v) Brass pump in system.

and copper. Brass and copper have about the same resistance. Aluminum coupled to other metals except steel becomes pitted. The range is from 5 to 17 mils after 10 months, the deepest pits occurring when the aluminum is coupled to copper. In general, it is best not to couple aluminum or magnesium to dissimilar metals (see Section H, Table 4).

Effect of Velocity

The effect of velocity on a clad aluminum alloy has been investigated using both tap water and synthetic waters(15) (see Section J, Table 4). This work showed that up to a maximum disk velocity of about 3000 ft/min little effect of velocity was found. Above this velocity, pitting and severe attack occurred. The velocity through an automobile radiator is of the order of 300-400 ft/min. Thus, velocity effects would not be expected to be a problem with aluminum in any systems now contemplated.

Effect of Heat Transfer

Heat transfer was studied through cast iron tubes in a laboratory simulated test apparatus.(16) The results show that under conditions of aeration and fluid flow, the corrosion rate increased from 220 to about 710 mils/year with a heat flux of 76,000 Btu/hr sq ft. When a brass pump was used in the system, the corrosion rate increased seven times (see Section K, Table 4).

This experiment shows that hot spots (estimated as high as 400 F)(6) or high heat-transfer rates in a cast iron engine can increase the corrosion significantly. This would not be true in a radiator which is at the coolant temperature and is transferring heat to the cooler air. In this case, the corrosion rate might be lower.

Inhibited Ethylene Glycol

Inhibitors may be used to reduce the rate of attack by a solution on metals. One way in which an inhibitor acts is to interfere with the electrochemical reation between the metal and the solution.

The anodic reaction in a corrosion cell is the formation of metal ions, e.g.:

$$M \dashrightarrow M^{+} + e.$$

The cathodic reaction can be the formation of hydrogen or hydroxyl ions, thus:

$$2\,H^{+} + 2\,e^{-} \dashrightarrow H_2$$

$$1/2\,O_2 + H_2O + 2\,e^{-} \dashrightarrow 2\,OH^{-}\,.$$

In a corrosion cell, electrons flow through the metal from the anode to the cathode. In solution the current normally is conducted by ions. Suppression of the anodic reaction is called anodic polarization and suppression of the cathodic reaction is called cathodic polarization. A combination of the two, mixed polarization, can also occur.

In ethylene glycol systems, the corrosion is controlled by the cathodic reaction. Reducing the anodic areas does not reduce the overall current flow (corrosion) but rather the attack of the remaining anodic areas is intensified and the result can be pitting. Therefore, anodic inhibitors must be used with care and in sufficient amount to ensure complete protection and freedom from pitting. For this reason anodic inhibitors are sometimes referred to as dangerous inhibitors.

Typical anodic inhibitors are:(18) borax ($Na_2B_4O_7$), disodium hydrogen phosphate (Na_2HPO_4), potassium and sodium dichromates ($K_2Cr_2O_7$), sodium benzoate (C_6H_5COONa), sodium hexametaphosphate ($(NaPO_3)_6$), sodium nitrite ($NaNO_2$), and sodium silicate (Na_2SiO_3). Cathodic inhibitors such as salts of zinc, nickel, manganese, and chromium are used for iron in neutral solutions while salts of arsenic antimony and mercury are used in acid solutions.

Organic inhibitors in general do not undergo chemical changes during inhibition as do many inorganic inhibitors. Polar organics such as amines, mercaptans, and others(18) are considered cathodic inhibitors and cause inhibition by adsorption on the metal surface. One example is mercaptobenzothiazole.

In a study on the polarization of steel, data are given for several inhibitors in 30 percent ethylene glycol at room temperature.(19) The data indicate that the following behave as anodic polarizers:

(1) Borax (1.0, 2.0%)
(2) Sodium nitrite (1/0, 1.5%)
(3) Sodium chromate (0.1, 0.25%)
(4) Sodium silicate (0.8%)
(5) Sodium benzoate (1.5%)
(6) Triethanolamine (1.5%).

Although amines are generally considered as cathodic polarizers adsorbing at cathodic areas, the data indicate that triethanolamine is primarily an anodic polarizer in tap water and 30 percent glycol. Mercaptobenzothiazole (0.1%) functions as a cathodic polarizer in an alkaline 1% borax solution. Sodium citrate (1.5%) and hydroquinone (0.5%) were found to be corrosion accelerators.

Commercial Inhibitors

The most common corrosion inhibitors which have found successful use in ethylene glycol solutions are listed below:

(1) Borax, usually with additives
(2) Sodium benzoate/sodium nitrite
(3) Triethanolamine (TEA)/sodium mercaptobenzothiazole (MBT).

These correspond somewhat to U. S. military and British standards:

FS O-A-548a FS O-1-490a	Borax 1.7, MBT 0.10, sodium phosphate 0.06
BS 3152	Borax 0.54
BS 3154	Sodium benzoate 1.2, sodium nitrite 0.1
BS 3150	TEA 0.4, phosphoric acid 0.19, MBT 0.041.

The U. S. antifreeze is based on 50 percent glycol while the British is based on 20 percent.

Many patented inhibitor systems issued since 1958 are based on the borax or borate inhibitor. Table 5 lists a number of these systems which may be in commercial use today. Note that many contain an addition of sodium mercaptobenzothiazole. No corrosion data have been included for these systems.

The following sections and tables discuss various inhibitor systems and give representative corrosion data.

Borax-Base Inhibitor

Borax-base inhibitors have been and are being used satisfactorily in ethylene glycol systems. Borax or sodium borate are not so effective alone as when combined with other inhibitors (see Table 6 for corrosion data).

A concentration of about 1 percent is generally used for effective inhibition by borax and sodium borate. In this concentration they are considered satisfactory for copper, brass, and solder but not acceptable for aluminum, steel, and cast iron.(6,10,36) Severe pitting of aluminum occurred when coupled or uncoupled to other metals at room temperature.(6) The British formulation BS 3152 (0.54 percent borax) is not considered to be as efficient as TEAP/MBT or sodium-benzoate/sodium-nitrite systems discussed later.(32,33)

Experiments have shown that borax is actually a corrosion accelerator at room temperature and below for galvanized steel.(9) Cadmium, brass, and magnesium also show increased corrosion rates in borax at 20 F. The attack on solder is slightly increased, copper is unaffected and lead is decreased at 20 F. Aluminum, steel, stainless steel, nickel, silver, tin, and titanium do not corrode appreciably in glycol or borax-inhibited glycol at 20 F.

A simulated "commercial" antifreeze containing borax, sodium benzoate, and sodium nitrite evinced fair protection of cast iron, aluminum, and bronze when nonaerated. When aerated, however, attack was severe.(32)

The U. S. Military uses a borax inhibitor for their vehicles. The concentrated antifreeze (FS O-A-548a) contains 2.5 percent borax. When diluted to 50 percent with water, an additional inhibitor (FS O-I-490) is added at a rate of 1/2 oz per quart of water This inhibitor is 95.5 percent borax and 3.5 percent MBT. This makes the inhibitor content of the antifreeze about 1.8 percent borax and 0.024 percent MBT.

A new specification, FS O-I-490a, calls for the addition of disodium phosphate to give added protection to aluminum in cooling systems. This inhibitor contains 75 percent borax, 15 percent MBT, and 10 percent disodium phosphate, and is added at the rate of 10 oz to 21 qt of water. This gives a concentration of about 1.7 percent borax, 0.10 percent MBT, and 0.06 percent Na_2HPO_4.

In 50 percent glycol at the above concentration, excellent protection is given to all cooling systems, including those containing aluminum alloys. However, the data shows that incomplete protection of aluminum and solder occurs if the inhibitor is used in distilled or tap water. As noted later, phosphates tend to cause sludge in hard water. Thus, this inhibitor may be most effective in soft or distilled water.

It is interesting to note that the military packages dry inhibitor for addition to make up water for glycol solutions because of problems that exist in prepackaging of antifreezes containing MBT.(37) Apparently the low concentration of MBT becomes depleted when stored in cans. It is pointed out, however, that many commercial antifreezes are packaged with the MBT added and no difficulties are reported.

Sodium Benzoate-Sodium Nitrite Inhibitor

Sodium benzoate inhibits glycol attack of mild steel, aluminum and solder but not cast iron.(6,38) The effectiveness of sodium benzoate is reduced considerably in the presence of high concentrations of chloride and sulfate ions, however(6) (for corrosion data see Table 7).

Sodium nitrite on the other hand, inhibits the attack of cast iron, as well as copper and brass. However, sodium nitrite increases attack of solder.(6,10)

Severe pitting attack is caused by sodium nitrite on aluminum, especially when coupled to other metals.(6) Sodium benzoate also causes pitting of aluminum when coupled to copper, brass, or solder.

TABLE 5. PATENT FORMULATIONS FOR BORATE-BASE ANTIFREEZE INHIBITORS

Percentages of Total Solution

Patent	Reference	Ethylene Glycol	Water	Borax, $Na_2B_4O_7 \cdot 10H_2O$	Sodium Metaborate, $NaBO_2$	Triisopropanolamine Borate	Magnesium Tetraborate	Boric Acid, H_3BO_3	CaO	Alkali Metal Arsenite, $NaAsO_2$	Sodium Monohydrogen Arsenite, Na_2HAsO_3	NaMBT[(a)]	Sodium Salt EDTA[(b)]	Other
U.S. 2,803,503	(20)			0.5 – 3.0						0.01 – 2.0[(c)]				0.01 – 2.0 benzothiazole
U.S. 2,803,604	(20)			0.5 – 2.5								0.01 – 2.0		Buffer to maintain pH at 7.5 – 10.5
U.S. 2,834,735	(21)								(0.1 H_2O)					Alkaline earth metal borate
U.S. 2,886,531	(22)	(40)	(60)					1.53	0.55					1.0 oil phase[(d)]
U.S. 2,937,145	(23)	94.3	4.10	1.33										0.1 g/1 phenolsulfonephthalein (dye) 0.25 NaOH
U.S. 2,960,473	(24)	Bal.			0.25 – 2.0						0.10 – 1.0	0.05 – 0.5		–
U.S. 3,015,629	(25)	96.48	2.13				1.26					0.13		–
U.S. 3,046,229	(26)	92.3						6.3	1.4					High-reserve alkalinity
U.S. 3,046,230	(27)	95.9	2.54		0.48	0.5				0.34		0.17		Green dye 0.001% polyglycol antifoam 0.10%
U.S. 3,079,343	(28)				(0.4 H_2O) 2 – 3								0.0003 – 3.00	0.05 – 500 ppm 2, 2 bipyridine, red color with iron
Brit. 921,320	(29)	95		(0.5 H_2O) 1.5 – 3.0								0.01 – 0.3		0.1 – 0.25 sodium silicate
Fr. 1,303,551	(30)	Bal.		5										0.2 colloidal SiO_2, antifoaming agent 0.05, plus dye
Ger. 1,045,173	(31)			Or $Na_5P_3O_{10}$								Yes		pH 7-8, may add EDTA or polymeric phosphoric acids and antifoam agents

(a) Sodium mercaptobenzothiazole.

(b) EDTA – ethylenediamine tetraacetic acid.

(c) Arsenate or molybdate.

(d) 39.6 napthalene-base lubricating oil; 29.8 basic barium sulfonate; 13.2 methylcyclohexyl thiophosphate; 8.4 sorbitan sesquioleate; 1.8 glycol monooleate; 6.6 zinc naphthenate; 1.1 sulfurized terpenes.

TABLE 6. BORAX-SYSTEM-INHIBITED ETHYLENE GLYCOL CORROSION

Glycol, %	Temp, F	pH	Aeration	Inhibitor, %	Reference	Corrosion, mils per year															
						Cu	Brass	Steel	Cast Iron	Solder	Al	Sn	Cd	Pb	SS	Mg	Ni	Ag	Ti	Zn	Other
20	176	8.2	No	Borax, 2.7	32				0.2												
20	176	8.0	No	Borax, 0.54	32,33				10		5-17 (Al-3Cu-0.6Mg-0.5Mn-0.7Si-0.4Fe)										3 (bronze)
50	140			Borax, 0.094	10				21		5										
50	212			Borax, 0.094	10				52		14 } No. 319										
50	284			Borax, 0.094	10				1		4										
50	-10			Borax, 1.0	9															1.3(a)	
50	20			Borax, 1.0	9	0.02	0.08			0.1			2.9	1.1		15				3.3(a)	
50	75			Borax, 1.0	9															1.6(a)	
50	170		Yes	Borax, 1.0	6,9	0.5	0.2	<0.2	<0.2	0.3	2.7									0.04(a)	
50(b)	170		Yes	Borax, 1.0	6	7.5	5.6	46	16	1.7	3.7										
50	180	7.4	Yes	Borax, 1.25	34	0.02	0.02	0.05	0.3	0.8	2.7										
50(b)	RT	7.4	No	Sodium borate, 1.0	6	Nil(c)	Nil(d)	2.6(e)	2.1(f)		3.7(f,g)										
50(b)	RT	7.4	No	Ditto	6	Nil(d)	Nil(c)	2.5(f)			3.9(e,g)										
50(b)	RT	7.4	No	"	6	Nil(h)	Nil(h)	0.04(c)	2.1(e)	0.2(f)	2.5(d,g)										
50(b)	RT	7.4	No	"	6	0.02(i)	0.03(i)		0.02(c)	0.2(e)	2.1(g,h)										
50(b)	RT	7.4	No	"	6	0.02(e)	0.04(f)	0.5(h)	1.3(d)	Nil	1.7(g,i)										
68(j)	180		Yes	Borax, 1.5	35	Nil	0.04	0.02	0.1	0.2(g)	1.1(g)										
0(k)	180		Yes	Borax, 0.1	36						130(l)										
0	180		Yes	Borax, 1.44 MBT, 0.06	8	Nil	Nil	Nil	Nil	1.4	53(g)										
50	180		No	Borax, 1.8 MBT, 0.024	34		Nil		Nil		1.1-0.2(m)										
50	180		No	Borax, 1.8 MBT, 0.024	34				Nil		, 0.02										
50	180		Yes	Borax, 1.8 MBT, 0.024	34	Nil	Nil	0.1	Nil	0.3	5.2										
68(j)	180		No	Borax, 1.5 Sodium phosphate, 0.03	35,37	Nil	Nil	Nil	Nil	0.2(g)	0.1-Nil										
20	176	7.5	No	Borax, 0.22 Sodium benzoate, 0.51; $NaNO_2$, 0.12	32				2.3		0.07 (Al-3Cu-0.6Mg-0.5Mn-0.7Si-0.4Fe)										0.5 (bronze)
20	176	7.5	Yes	Ditto	32				73		18										7 (bronze)
0	180	8.9	Yes	Borax, 1.0 MBT, 0.2, sodium phosphate, 0.12	37	Nil	Nil	Nil	Nil	0.3	8										
0(k)	180		Yes	Borax, 1.0 MBT, 0.2, sodium phosphate, 0.12	37	Nil	Nil	Nil	Nil	3.8	33										
50	180		Yes	Borax, 1.7 MBT, 0.10, sodium phosphate, 0.06	34,37	Nil	Nil	Nil	Nil	Nil	0.3										
50	180		No	Borax, 1.5 MBT, 0.10, sodium phosphate, 0.06	37	Nil	Nil	Nil	Nil	0.03	Nil										
50	180		No(n)	Borax, 1.6 MBT, 0.09, sodium phosphate, 0.05	35		Nil		Nil		Nil										
50(o)	180	7.5	Yes	Borax, 1.5 MBT, 0.10, sodium phosphate, 0.06	37	Nil	0.02	Nil	0.2	0.2	0.07										
68(j)	180	7.2	Yes	Borax, 2.5 MBT, 0.20 sodium phosphate, 0.12	37	Nil	Nil	Nil	Nil	0.02	0.1										

(a) Galvanized steel.
(b) Tap water plus 2 g/l NaCl and 1 g/l Na_2SO_4.
(c) Coupled to aluminum.
(d) Coupled to steel.
(e) Coupled to brass.
(f) Coupled to copper.
(g) Pitting.
(h) Coupled to cast iron.
(i) Coupled to solder.
(j) Military arctic-type antifreeze.
(k) Tap water, or synthetic hardwater.
(l) 1-1/2"-dia Al clad disk rotated at 4700 ft/min. Note flow rate in automobile radiator 300-400 ft/min.
(m) Decreases with time (1000-2000-hr)
(n) 2000-hr simulated service.
(o) Hard water containing 342 ppm $CaCO_3$.

TABLE 7. SODIUM BENZOATE-SODIUM NITRITE INHIBITED ETHYLENE GLYCOL

						Corrosion, mils per year															
Glycol, %	Temp, F	pH	Aeration	Inhibitor, %	Reference	Copper	Brass	Steel	Cast Iron	Solder	Al	Tin	Cd	Pb	SS	Mg	Ni	Ag	Ti	Zn	Other
50	20			Sodium benzoate, 1.0	9															0.8(a)	
50(b)	170	7.6	Yes	Ditto	6	1.9	2.7	<0.2	10	0.9	0.5										
50(c)	170	7.4	Yes	"	6	27	12	46	11	2.8	1.6										
50(c)	RT	7.6	No	Sodium benzoate, 1.0	6	Nil(d)	Nil(e)	1.8(f)			2.2(g,h)										
50(c)	RT	7.6	No	Ditto	6	Nil(i)	Nil(d)	1.3(j)	0.2(e)	0.2(g)	1.1(f,h)										
50(c)	RT	7.6	No	"	6	Nil(j)	Nil(j)	1.2(d)	2.0(f)		0.1(e,h)										
50(c)	RT	7.6	No	"	6	Nil(e)	0.02(i)	1.9(g)	1.1(d)	0.1(f)	0.2(h,j)										
50(c)	RT	7.6	No	"	6	Nil(f)	0.1(g)		2.0(g)	Nil(d)	0.4(h,i)										
0(b)	180		Yes	Sodium benzoate, 3.0	36						10(h,k)										
0(b)	180		Yes	Sodium benzoate, 0.3	36						>80(h,k)										
20(b)	176(l)		No	Sodium nitrite, 0.1	38		0.8														
20(b)	176(l)		No	Sodium nitrite, 1.5	38		4													0.2(a)	
50	20			Sodium nitrite, 1.0	9																
50(b)	170			Ditto	6	0.5	0.2	<0.2	0.2	4.5	0.5										
50(c)	170			"	6	3.2	0.2	<0.2	0.4	3.3	0.5										
50	140			Sodium nitrite, 0.064	10				1.2		0.3	Al 319									
50	212			Ditto	10				Nil		3.2										
50	284			"	10				0.7		22										
50(c)	RT	7.2		Sodium nitrite, 1.0	6	Nil(d)	0.04(g)	Nil(f)			3.7(g,h)										
50(c)	RT	7.2		Ditto	6	0.02(i)	Nil(d)	0.1(f)	0.1(e)	4.1(g)	4.1(f,h)										
50(c)	RT	7.2		"	6	0.03(j)	0.02(j)	0.03(d)	0.1(f)		3.6(e,h)										
50(c)	RT	7.2		"	6	0.04(e)	Nil(i)	0.5(g)	Nil(d)	8.5(f)	2.5(h,j)										
50(c)	RT	7.2		"	6	0.02(f)	1(g)		0.6(g)	0.1(h)	0.5(h,i)										
0(b)	180		Yes	Sodium nitrite, 0.03	36						15(h,k)										
0(b)	180		Yes	Sodium nitrite, 3.0	36						40(h,k)										
20(b)	176(m)		No	None	38		2		20												
20(b)	176(m)		No	Sodium Benzoate, 1.5	38		0.4		10												
20(b)	176(m)		No	Sodium nitrite, 0.1	38		8		0.3												
20(b)	176(m)	6.8	No	Sodium benzoate, 1.5 Sodium nitrite, 0.1	33,38		0.2		0.3												
20(b)	-(n)	8.4	No	Sodium benzoate, 1.5 Sodium nitrite, 0.1	39		0.05(i,n)		0.1(n)		0.3-1.3(j,n,o)										1 bronze (1.2 Sod. B. 0.1 Sod. N.)
33(b)	140(m)	8.5	No	Sodium benzoate, 1.5 Sodium nitrite, 0.1	14	0.1			0.02			0.3(p)		0.1(q)							
20(b)	RT	8.1	No	Sodium benzoate, 1.5 Sodium nitrite, 0.1	14		Nil(i)		(r)												
30(b)	RT	8.1	No	Sodium benzoate, 1.5 Sodium nitrite, 0.1	13		Nil(i)		(r)												
25(b)	RT	8.5	No	Sodium benzoate, 5.0 Sodium nitrite, 0.3	13	0.02	0.01(i)	Nil	Nil(d,g)		Nil(g)	Al and 94Al-2.3Si-1.2Cu-1Fe-0.9Ni-0.1Mg									
25(b)	176(m)	8.5	No	Sodium benzoate, 5.0 Sodium nitrite, 0.3	13	0.05	0.04(i)	Nil	0.2(d,g)		Nil(g)	Al and 94Al-2.3Si-1.2Cu-1Fe-0.9Ni-0.1Mg									

(a) Galvanized steel.

(b) Tap water.

(c) Tap water containing 2 g/l NaCl and 1 g/l Na_2SO_4.

(d) Coupled to aluminum.

(e) Coupled to steel.

(f) Coupled to brass.

(g) Coupled to copper.

(h) Pitting.

(i) Coupled to solder.

(j) Coupled to cast iron.

(k) 1-1/2"-dia No. 100 Al-Zn clad disk rotated at 4700 ft/min. Note flow rate in auto radiator 300-400 ft/min

(l) Intermittent heating, approximately 8 hr/day, 5 days/wk.

(m) l plus agitation.

(n) Auto and truck service tests 2500 miles, test coupons replaced thermostats, corrosion listed as mils penetration.

(o) Corrosion increase as pH rose from 8 to 11.

(p) On steel.

(q) Lead plate containing 20 percent tin on steel.

(r) Some corrosion.

Sodium benzoate slightly increases the attack of galvanized steel at 20 F, the same way as the borax inhibitor.(9) Under high-velocity conditions, sodium benzoate is marginal and sodium nitrite accelerates attack of aluminum.(36)

For effective inhibition of the steel and cast iron in engine cooling systems, a combination of 1.5 percent sodium benzoate, 0.1 percent sodium nitrite is used.(13,14,32,38,39) However, this protection is conferred on cast iron only if the solution is first heated.(13,38) Complete protection of the system is obtained for room-temperature exposure as well as engine-cooling system temperature if the concentrations are raised to 5 percent sodium benzoate and 0.3 percent sodium nitrite. Less glycol is then needed since the benzoate is about as effective as glycol in lowering the freezing point of water.(13) Corrosion of aluminum was found to increase slightly as the pH of the solution rose from 8 to 11. Thus, complete protection of aluminum may not be obtained with this inhibitor.

It has been suggested that the 1.5-.1 inhibitor causes deterioration of neoprene rubber.(32)

Triethanolamine Phosphate/Sodium Mercaptobenzothiazole System

Triethanolamine phosphate (TEAP) is obtained by adding about 2 parts of triethanolamine (TEA) to 1 part phosphoric acid (H_3PO_4). TEAP inhibits the corrosion of many metals but promotes the corrosion of copper.(14,17) TEAP stabilizes the copper ions formed so that they can diffuse through the glycol water system mixture to deposit on steel or aluminum surfaces. This deposit causes corrosion of both metals and pitting of aluminum. It has been shown that copper is not deposited on aluminum in a pure glycol system.(17) This effect of copper deposition would also be expected with other light metals such as magnesium (for corrosion data, see Table 8).

TEAP, by itself, is not a very effective inhibitor for cast iron, copper, aluminum, or magnesium.

Sodium mercaptobenzothiazole (MBT) inhibits copper and its alloys by the precipitation of a chocolate-brown copper compound on the

TABLE 8. TRIETHANOLAMINE PHOSPHATE, SODIUM MERCAPTOBENZOTHIAZOLE-INHIBITED ETHYLENE GLYCOL CORROSION

Glycol, %	Temp, F	pH	Aeration	Inhibitor, %	Reference	Corrosion, mils per year															
						Copper	Brass	Steel	Cast Fe	Solder	Al	Tin	Cd	Pb	Stainless Steel	Mg	Ni	Ag	Ti	Zn	Other
33[a]	140[b]	7	No	H_3PO_4 1.0 + TEA (about 2.1) to make TEAP at pH 7 (about 3.1)	14	1.6			2.2			0.01[c]	0.8[d]	0.7[e]	Nil(18-8)						
100	RT	7	No	TEAP 2.0	17	1.4		9													
30	RT	7	No	TEAP 2.0	17	1.4					1.0										
20	176	7.0	No	H_3PO_4 0.19, TEA 0.4	33				8		32	Al and 83Al-8Cu-4Si-2Zn casting									13 bronze
60	239			Prestone antifreeze (possibly TEAP type)	12											4[f] (Mg-6Al-0.2Mn)					
60	239			Prestone + NaF 0.1	12											18[f] (Mg-6Al-0.2Mn)					
95	261			Air Corps Prestone (TEAP type)	12											6[g] (Mg-8.5Al-0.5Zn-0.2Mn)					
50[a]	170	9.5	Yes	Sodium mercaptobenzothiazole MBT 1.0	6	<0.2	Nil	<0.2	2.4	0.5	<0.5										
50[h]	170	9.5	Yes	MBT 1.0	6	<0.2	Nil	36	9.4	0.7	<0.5										
50[h]	RT	9.5	No	MBT 1.0	6	Nil[i]	Nil[f]	1.1[j]			0.5[k,l]										
50[h]	RT	9.5	No	MBT 1.0	6	Nil[m]	Nil[i]	0.8[n]	0.3[f]	Nil[k]	0.3[j,l]										
50[h]	RT	9.5	No	MBT 1.0	6	Nil[n]	Nil[n]	0.03[i]	0.8[j]		1.9[f,l]										
50[h]	RT	9.5	No	MBT 1.0	6	Nil[f]	Nil[m]	1.0[k]	0.03[i]	Nil[j]	1.9[l,n]										
50[h]	RT	9.5	No	MBT 1.0	6	Nil[j]	Nil[k]		0.6[k]	Nil[i]	Nil[m]										
20	176	7.0	No	H_3PO_4 0.19, TEA 0.4, MBT 0.041	32,33				0.8		0.7	Same as Ref. (33) above									0.04 bronze
33	140[b]	7	No	H_3PO_4 1.0, TEA ~2.1, MBT 0.2	14	Nil			0.6			Nil[c]	0.4[d]	0.1[e]	0.003						
62.5	-30,RT,135			TEAP 1.6, MBT 0.09	40						<0.02	(5052-T6, 6061-T6)									

(a) Tap water.
(b) Intermittent heating ~8 hr day, 5 days/week.
(c) On copper.
(d) On Steel.
(e) Lead plate containing 20 percent tin on steel.
(f) Coupled to steel.
(g) No galvanic acceleration when coupled to steel.
(h) Tap water containing 2 g/l NaCl and 1 g/l Na_2SO_4.
(i) Coupled to aluminum.
(j) Coupled to brass.
(k) Coupled to copper.
(l) Pitting.
(m) Coupled to solder.
(n) Coupled to cast iron.

surface.(4) It is an effective inhibitor of copper, brass, steel, solder, and aluminum, and a fair inhibitor for cast iron. However, its effectiveness on steel and cast iron is seriously reduced in very high chloride and sulfate water (2g/l NaCl, 1g/l Na_2SO_4).(6)

In galvanic tests at room temperature, MBT caused severe pitting of aluminum when coupled to copper, brass, steel, and cast iron.

MBT is not very soluble in cold water and sometimes precipitates on container walls. It redissolves readily in hot water. Its upper limit of solubility in 30 percent glycol is suggested as 0.1 percent.(41)

With the combination inhibitor, TEAP and MBT, the corrosion of copper and its alloys is inhibited and the corrosion of aluminum, lead, and iron in contact with it is much reduced.(14,32,41) Of the metals tested, aluminum, brass, aluminum brass, leaded brass, copper, solder, nickel, chromium, and stainless steel, only nickel was adversely affected.(41)

Soluble Oil

Soluble oil has frequently been suggested as a corrosion inhibitor by itself(32) with buffers(36) and with borax.(4) However, there are many types of soluble oils which may behave differently in various systems. Many soluble oils which are excellent metallic corrosion inhibitors swell rubber severely.(42)

One soluble oil was found to be a poor corrosion inhibitor and caused pitting of aluminum.(32,33) Another was found to inhibit steel, brass, copper, aluminum, and cast iron but not solder.(6) At room temperature, severe pitting of aluminum occurred when coupled to copper, brass, steel, cast iron, and solder.(6) (see Table 9 for corrosion data).

However, in high-velocity tests with aluminum, a soluble oil was found to be quite effective except in high-chloride and high-alkaline waters.(36) When a buffer was added to the soluble oil, an extremely effective inhibitor was obtained.

Chromate Inhibitor

Chromates have long been used as effective inhibitors for water in diesel and other engines.(42) However, considerable supervision is sometimes required to maintain the concentration at safe levels. For aluminum protection, concentrations of 0.1 percent are recommended. With heavy metal ions such as copper present, concentrations of 10 times that may be required for protection.(43) For magnesium in chloride water, a concentration of 10 percent of the chloride content is required for protection.

TABLE 9. SOLUBLE OIL-INHIBITED ETHYLENE GLYCOL CORROSION

Glycol, %	Temp, F	pH	Aeration	Inhibitor, %	Reference	Corrosion, mils per year															
						Copper	Brass	Steel	Cast Fe	Solder	Al	Tin	Cd	Pb	Stainless Steel	Mg	Ni	Ag	Ti	Zn	Other
20	176	8-10	No	"Dromus D"(a), soluble oil .5	32,33				7		33(b)	Al and 83Al-8Cu-4Si-2Zn casting									10 bronze
50(c)	170	8.3	Yes	Soluble oil, 1.0	6	<0.2	0.3	<0.2	2.4	0.5	<0.5										
50(d)	170	7.8	Yes	Ditto	6	<0.2	0.3	<0.2	9.4	0.7	<0.5										
50(d)	RT	8.3	No	Soluble oil, 1.0	6	0.01(e)	0.02(f)	0.1(g)	0.03(h)		0.9(b,h)										
50(d)	RT	8.3	No	Ditto	6	Nil(i)	0.03(e)	Nil(i)	0.1(f)		0.9(b,g)										
50(d)	RT	8.3	No	"	6	0.02(j)	0.02(i)	0.02(e)	0.1(g)	0.1(h)	1.1(f,b)										
50(d)	RT	8.3	No	"	6	0.01(f)	0.02(j)	0.03(h)	0.04(e)	0.1(g)	1.1(b,i)										
50(d)	RT	8.3	No	"	6	0.1(g)	0.04(h)			Nil(e)	0.1(b,j)										
0(c)	180		Yes	Soluble oil and trisodium phosphate, 3.0	36						Nil(k)										
0(c)	180		Yes	Ditto	36						1.6(l)										
0(c)	180		Yes	Soluble oil, 0.625	36						0.6(l)										
50(c)	180		Yes	Soluble oil and TSP, 3.0	36						0.5(l)										
50(c)	180	6	Yes	Soluble oil, 1.0	36						0.6(l)										
50(c)	180	8	Yes	Ditto	36						3(l)										
50(c)	180	11	Yes	"	36						10(l)										
0(c)	180		Yes	Soluble oil, 1.0, buffer(m), 0.8	36						2-3(k)										
0(c)	180		Yes	Ditto	36						Nil(l)										
50(c)	180		Yes	"	36						Nil(k,l)										
50(c)	180	6	Yes	Soluble oil, 1.0, buffer(m), 0.8	36						0.6(l)										
50(c)	180	8	Yes	Ditto	36						1.4(l)										
50(c)	180	11	Yes	"	36						Nil(l)										

(a) Trademark Shell-Mex and B.P. Ltd.
(b) Severe pitting.
(c) Tap water.
(d) Tap water plus 2 g/l NaCl and 1 g/l Na_2SO_4.
(e) Coupled to aluminum.
(f) Coupled to steel.
(g) Coupled to brass.
(h) Coupled to copper.
(i) Coupled to cast iron.
(j) Coupled to solder.
(k) 1-1/2"-dia No. 100 Al-Zn clad disk stagnant and rotated at 390 ft/min.
(l) See k but at 4700 ft/min.
(m) 55% of 2M KH_2PO_4 – 45% 2M NaOH.

Chromates have also been suggested for use as glycol solution corrosion inhibitors. It had been reported, however, that chromate could not be used with glycol because of oxidation of the glycol by the chromate and resultant sludge formation.(6) Qualitative tests have shown that the rate of reaction is dependent on heat, pH, and the catalyzing effect of light. The reaction rate increases with a temperature increase, a decrease in pH, or the presence of light. The trivalent chromium compound is soluble in solutions having a pH above 8 and increasingly insoluble below 8. With light, a glycol solution containing chromates changes from a yellow, "safe" color to green or "unsafe" color.(44)

In tests conducted in light,(6,12,36) inhibitive effects of chromates are shown in short-term tests. Potassium chromate is satisfactory for copper, brass, solder, cast iron, and steel, and fair with aluminum. It is only fair for steel and cast iron when in contact with copper and brass. Some pitting also occurs on aluminum coupled to other metals. Test results are summarized in Table 10.

In velocity tests conducted on aluminum, sodium dichromate was found to be an effective inhibitor in water, but only fair in glycol.(36)

In automotive road tests, protection was maintained with sodium chromate, but analysis of chromate after 8 months (5.4 ppm) indicated that regular additions are required for adequate protection, i.e., a concentration of 500 ppm or more. The author states that chromates are not recommended for use unless thoroughly tested.(44)

Miscellaneous Inhibitors

Various other chemicals have been examined as inhibitors for glycol. At room temperature, sodium acetate was found to slightly accelerate and sodium carbonate slightly reduce the corrosion of galvanized steel(9) (see Table 11 for corrosion results).

Potassium sulfide has been listed in British Patent 381,088 as a possible inhibitor for magnesium in glycol. The weight loss was reduced from 19.6 grams per square meter to nil(43) (other suggested inhibitors are shown in Table 12).

In tests of inhibitors for commercial dehumidification towers, various chemicals as listed in Table 11 have been found effective in reducing vapor-phase corrosion of steel.(5)

In high-velocity tests, disodium phosphate and sodium silicate were found to be effective inhibitors for aluminum.(36) Sodium silicate, however, caused excessive foaming, and phosphates can precipitate sludge when hard water is

TABLE 10. CHROMATE-INHIBITED ETHYLENE GLYCOL CORROSION

Glycol %	Temp, F	pH	Aeration	Inhibitor, %	Reference	Corrosion, mils per year															
						Copper	Brass	Steel	Cast Fe	Solder	Al	Tin	Cd	Pb	Stainless Steel	Mg	Ni	Ag	Ti	Zn	Other
50$^{(a)}$	170	6.2	Yes	Potassium dichromate, 1.0	6	<0.2	<0.2	<0.2	0.2	0.2	<0.5										
50$^{(b)}$	170	6.2	Yes	Ditto	6	<0.2	<0.2	<0.2	0.2	0.2	<0.5										
50$^{(b)}$	RT	6.1	No	"	6	Nil$^{(c)}$	Nil$^{(d)}$	0.4$^{(e)}$			0.3$^{(f,g)}$										
50$^{(b)}$	RT	6.1	No	"	6	Nil$^{(h)}$	Nil$^{(c)}$	0.02$^{(i)}$	Nil$^{(d)}$	Nil$^{(d)}$	0.1$^{(e,g)}$										
50$^{(b)}$	RT	6.1	No	"	6	Nil$^{(i)}$	Nil$^{(i)}$	0.03$^{(c)}$	0.5$^{(e)}$		0.1$^{(d,g)}$										
50$^{(b)}$	RT	6.1	No	"	6	Nil$^{(d)}$	Nil$^{(h)}$	0.2$^{(f)}$	Nil$^{(c)}$	Nil$^{(e)}$	0.4$^{(g,i)}$										
50$^{(b)}$	RT	6.1	No	"	6	Nil$^{(e)}$	Nil$^{(f)}$		0.3$^{(f)}$	Nil$^{(c)}$	0.05$^{(g,h)}$										
0	RT			Sodium dichromate, 1.0	12											1.3$^{(d)}$					
0$^{(a)}$	100		Yes	Sodium dichromate, 0.625	36						Nil$^{(j)}$										
50$^{(a)}$	100		Yes	Ditto	36						10$^{(g,j)}$										

(a) Tap water.
(b) Tap water containing 2 g/l NaCl and 1 g/l Na_2SO_4.
(c) Coupled to aluminum.
(d) Coupled to steel.
(e) Coupled to brass.
(f) Coupled to copper.
(g) Pitting.
(h) Coupled to solder.
(i) Coupled to cast iron.
(j) 1-1/2"-dia No. 100 Al-Zn clad disk rotated at 4700 ft/min.

TABLE 11. MISCELLANEOUS INHIBITORS FOR ETHYLENE GLYCOL

						Corrosion, mils per year															
Glycol, %	Temp, F	pH	Aeration	Inhibitor, %	Reference	Copper	Brass	Steel	Cast Fe	Solder	Al	Tin	Cd	Pb	Stainless Steel	Mg	Ni	Ag	Ti	Zn	Other
50	20		No	Sodium acetate, 1.0	9															0.6[(a)]	
50	20		No	Sodium carbonate, 1.0	9															0.08[(a)]	
?	212			Potassium sulfide, 0.1	43											Nil					
92.5	295		No	None	5			125[(b)]													
92.5[(c)]	295		No	–[(c)]	5			0.2[(b)]													
92.5	295		No	NaOH, 0.2, or K_2HPO_4, 0.2, or K_2HPO_4 and NaCl, 0.2 each, or tetraethylene-pentamine, 0.05, or Na_2HPO_4, 0.05	5			<.4[(b)]													
92.5	295		Yes	K_3PO_4, 0.025, or K_2HPO_4, 0.025	5			2.4[(b)]													
92.5	295		Yes	TEAP, 0.025	5			1.0[(b)]													
92.5	295		Yes	Monoethanolamine, 0.025, or N_2H_4, 0.20	5			0.1[(b)]													
0[(d)]	180		Yes	Na_2HPO_4, 0.03	36						1.3[(e)]										
50[(d)]	180		Yes	Ditto	36						Nil[(f)]										
0[(d)]	180		Yes	Sodium silicate, 3.0	36						0.2[(e)]										
50[(d)]	180		Yes	Ditto	36						Nil[(f)]										

(a) Galvanized steel.
(b) Vapor phase, <0.6 mpy immersed in liquid phase.
(c) Solution put through hydroxyl ion-exchange resin.
(d) Tap water.
(e) 1-1/2"-dia. No. 100 Al-Zn clad disk rotated at the following velocities: static, 390 and 4700 ft/min.
(f) Same as (e) except 4700 ft/min only.

used. Thus, neither is very applicable for automotive coolant inhibitors.

TABLE 12. MISCELLANEOUS INHIBITORS FOR ETHYLENE GLYCOL(45)

Metal	Inhibitor	Ref.
Aluminum	Sodium tungstate or molybdate	46
Aluminum	Alkali borates or phosphates	47
Aluminum	Sodium nitrate, 0.01-1.0%	48
Aluminum	Sodium cinnamate 2% + sodium tetrasilicate 0.1% + phosphoric acid to pH 9.5	49
Brass, copper, steel	Alkali borates and phosphates	50
Cadmium-plated steel	Sodium fluorophosphate, 1%	51
Galvanized iron, steel	Trisodium phosphate, 0.025%	51
Magnesium	Alkaline metal sulfides	43

Salts such as calcium bicarbonate and sodium silicate inhibit corrosion but may form deposits which can impair heat transfer.

Depletion of Corrosion Inhibitors

Corrosion inhibitors loose their effectiveness as their concentration is lowered and they become depleted in an automobile cooling system. Under normal driving conditions, commercial inhibitors may retain their effectiveness for a year or more. However, inhibitors are more rapidly depleted under conditions such as when:

(1) the cooling system was initially rusty,

(2) high-speed engine operation is used, or

(3) excessive aeration of the coolant occurs.

In modern pressurized cooling systems, the latter is not likely to occur unless the coolant level is maintained too low.

One of the best overall inhibitor systems appears to be the U. S. Military system of borax, MBT, and phosphate. Measurements of pH and reserve alkalinity show good protection after 2000 hours of continuous operation at 180 F in simulated service tests using 50 percent glycol/distilled water. In field tests with 30 percent glycol/distilled water in two 5-ton trucks, adequate protection was maintained for 6 weeks, when the tests were discontinued. With two 1960 automobiles and the same solution, satisfactory performance was observed after 15 months' operation and mileage of 24,000 to 34,000 miles.(37) Note that in hard water, the phosphate may be depleted due to sludge precipitation.

In aircraft-engine coolant tests with TEAP/MBT, effective operation was maintained for 8 to 16 months before the MBT concentration fell from 0.09 to 0.01 percent. In automotive service, 12 months was regarded as a conservative life although no phosphate could be detected and the MBT was just a trace.(41) In later field tests, the phosphate and MBT content had fallen to a tenth to a third of the original concentration in 2 months or 4000 to 5000 miles.(4,16) Some rust was also detected in diesel and gasoline engine trucks after 4000 to 8000 miles even though the pH values did not necessarily drop. These results suggest that pH is not as good measure of the corrosiveness of the glycol. The results suggest that the solution is corrosive when the acid content exceeds the base content, even though the pH may still be neutral.(4)

The effectiveness of 1.5 sodium benzoate and 0.1 sodium nitrite has been shown in automobile tests in new and rusted engines. In several tests of 2500 miles, the inhibitors were found to keep corrosion of cast iron, steel, copper, brass, and solders at low levels, and to minimize entrained rust in the solution. The pH values changed from about 8 to 9 or 10. In the high-pH solutions, corrosion of aluminum was observed (see Table 7).

In simulated service tests, the concentration of sodium nitrite dropped to about a tenth of initial concentration and the sodium benzoate stayed about the same after 800 hours. The pH changed from slightly above 7 to slightly below.(32)

In similar simulated service tests, with 0.54 percent borax, the pH began to drop after 500 hours and reached 7.5 at 1000 hours. Protection was still maintained, however. Acidic compounds formed after about 500 hours and once the buffering action of borax was neutralized, excessive corrosion would be expected.(32)

The soluble oil used in these simulated service tests was not effective, and corrosion was noted after 700 hours.(32)

In 8-month automotive tests, the sodium chromate content was reduced from 2000 to 5.4 ppm. The pH rose during the same period from 8.3 to 10.5. Where chromate was added continuously from a filter, a "safe" level of 451 ppm was maintained at a pH of 8.8.(44)

Reasonable service might be expected for the military borax-base inhibitor of over a year or over 20,000 miles with distilled water, up to 12 months or 4000 to 5000 miles for TEAP/MBT, over 2500 miles or 1000 hours of service for benzoate/nitrite. The service life for a given soluble oil must be determined individually. The service life of a single addition of chromate might be 8 months, depending on the initial concentration.

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APPENDIX A

TEST PROCEDURES USED IN ETHYLENE GLYCOL STUDIES

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TEST PROCEDURES USED IN ETHYLENE GLYCOL STUDIES

The test procedures used to obtain the data presented are mainly of three types: (1) laboratory glassware tests, (2) laboratory simulated service conditions, and (3) service conditions. A description of all three follows.

Laboratory Tests in Glassware

Most of the corrosion data which are presented were obtained from controlled laboratory tests in glassware. The most reproducible results are obtained by this method, although they are not necessarily indicative of actual service conditions. Many of the variables found in service conditions can be controlled in the laboratory tests. Such variables are concentration, temperature, pH, aeration, impurities, metals in system, galvanic coupling, velocity, and heat transfer.

The simplest and most straightforward test is that in which the solution is made up using distilled water, placed in glassware, and heated to temperature. The specimen is cleaned and weighed and placed on test (only one alloy to a container) for a specified time, usually from 2 days(17) up to 1 to 4 weeks.(5) (See References 5, 10, 11, 12, 17, 18, 19, and 44.)

A slight variation from the above test is when air is bubbled into the solution to saturate it in oxygen, as described in Reference 9. As expected, the corrosion rates in an aerated system are higher than in nonaerated.

A more sophisticated apparatus(7) used individual specimens exposed 48 to 96 hours. The flask had inlets through which gas and liquid were metered, and the solution was thus either aerated or nonaerated and could be continuously renewed by adding new solution. The results presented in the tables are for the most corrosive condition, i.e., aeration combined with solution renewal.

Another test method used a technique similar to that of service conditions, in that all metals and alloys were placed in the same container, although not in contact. Thus, any interaction of ions under service conditions should also occur in the test. The tests were aerated and run for 192 hours.(8,34,35,37)

In other test procedures, tap water, either that of the locale or synthetic, was used to obtain the effect of impurities in the test.(1,6,13-15,36,38) The chloride, sulfate, and carbonate ions were most often used in synthetic tap water. Chloride contents from 15 to 2000 ppm, and sulfate to 1000 ppm were used. Hardness of tap waters ranged from 100 to over 300 ppm. Chloride content of the tap waters ranged from 10 to over 50 ppm.

Reference 1 used tap water in a simple flask with aeration.

Reference 6 used tap water and a high chloride and sulfate synthetic water. The specimens were individually rotated vertically at 100 rpm in the solution for 14 days at the test temperature. For galvanic couple tests, the couple and individual specimens of the two were placed in one container under static conditions at room temperature.

For high-velocity tests,(15,36) a 1-1/2-inch-diameter disk of Alclad material (No. 100, Al-Zn clad) was rotated in an open beaker in a horizontal plane. Considerable aeration probably occurred. The author stated that most of the corrosion occurred on the top side of the disk, starting at the edges, the point of maximum velocity.

References 13, 14, and 38 used tap water with 320-ppm hardness. In preliminary experiments, specimens were exposed individually in a simple tube for 28 days.(13,38) Other experiments used intermittent heating for periods of 8 to 9 hours with cooling overnight and on weekends to simulate actual operation. All alloys were exposed in the same beaker, and a stirrer was used to maintain agitation. These specimens were exposed 12 to 135 days. Corrosion rates were based on total exposure time.

In room-temperature tests with stagnant tap water, soldered joints and galvanic couples were exposed 3 and 5 years, respectively.

Laboratory-Simulated Service Conditions

Laboratory devices to simulate engine cooling systems usually contain a circulating pump, a reservoir to simulate the engine block, and possibly a small radiator. The system is often enclosed, but sometimes has means to permit some aeration of the coolant.

The apparatus used in Reference 6 consisted of a cast-iron block heated by strip heaters, a small radiator, and an electric motor-driven pump. A fan was used on the radiator and the coolant flow was regulated by a thermostat. Intermittent heating was used to simulate service. Synthetic tap water was employed. However, only qualitative data were obtained from this system, since weighed test specimens were not included.

References 34, 35, and 37 used a cast-iron or aluminum block and an aluminum or brass radiator. A circulating pump, probably of cast iron, was used in a closed system. Weighed rods were inserted into the radiator to obtain corrosion data. Several alloys were exposed in the same system. Tests were run with either distilled or synthetic tap water for periods of 2000 hr.

Another system was designed to obtain heat-transfer data. This system consisted of a plastic pump, a cast-iron block, a coolant reservoir, a heating leg, and a neoprene specimen section. The specimens were short tubes through which the coolant flowed. Heat transfer was obtained by heating the specimens externally. Two degrees of aeration were obtained by placing the coolant discharge tube either above the surface of the water or beneath it. Only maximum aeration corrosion rates are reported, since minimum aeration (2 ppm O_2) data should not be compared with conditions of no aeration. Distilled and deionized water was used. Heat-transfer studies with cast iron were run for 100 hours.(16) Other studies with multiple alloys in the same system were run for 1000 hours.(32,33)

Other types of laboratory equipment to simulate service are discussed in Reference 1, although no quantitative data are given. These tests consisted of actual test engines run on a dynamometer. Such tests are usually reserved to prove out systems developed in simpler and less expensive laboratory tests.

Service Tests

In service tests, formulations which appeared attractive in laboratory tests were used in automobiles and trucks actually in service. The results were usually in the form of satisfactory or unsatisfactory service and length of time used. The pH, acid content, and makeup water were recorded as a function of mileage and time.(1,4,37,39) Where possible, the amount of inhibitor was measured as in Reference 4.

Some quantitative results were obtained by inserting specimens in the engine of the test vehicles in place of the thermostat.(39) However, the actual temperature of the coolant was variable because of the removal of the thermostat and was not recorded. Also, the length of exposure in hours was not recorded. The tests lasted about 2500 miles.

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13. ABSTRACT

Solutions of ethylene glycol are being considered as heat-transfer media for radiators in manned space capsules. This report was prepared to summarize the available corrosion data on uninhibited and inhibited ethylene glycol solutions. Much of the corrosion data are based on automotive and diesel engine coolant systems.

Several factors considered are: time dependence, effect of pH, concentration, temperature, aeration, chloride ion, velocity, heat-transfer rate, and galvanic couples.

Inhibitors for which corrosion data are presented include: borax, sodium benzoate, sodium nitrite, triethanolamine, sodium mercaptobenzothiazole, soluble oil, chromates, as well as miscellaneous inhibitors. A number of patented inhibitors based on borax are discussed.

Descriptions of test procedures including automobile service tests are presented.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Application	8	3				
Heat-transfer media	9	3				
Ethylene glycol	9	3	1,3	3		
Radiators	4	3	1,9	3	4	
Space capsules	4	3			4	
Manned	0				0	
Corrosion			8,7	3		
Copper alloys			1,9		9	
Aluminum alloys			1,9		9	
Steel			1,9		9	
Cast iron			1,9		9	
Solders			1,9		9	
Magnesium			1,9		9	
Stainless steel			1,9		9	
Tin			1,9		9	
Lead			1,9		9	
Cadmium			1,9		9	
Nickel			1,9		9	
Titanium			1,9		9	
Zinc			1,9		9	
Precious metals			1,9		9	
Graphite			1,9		9	
Uninhibited			0			
Inhibited			0			
Time			6			
pH			6			
Concentration			6			
Temperature			6			
Aeration			6			
Chloride ions			6			
Velocity			6			
Heat-transfer rate			6			
Galvanic couples			6			
Protection					8	3
Inhibitors					10	
Borax					10	
Sodium benzoate					10	
Sodium nitrite					10	
Triethanolamine					10	
Sodium mercaptobenzothiazole					10	
Soluble oil					10	
Chromates					10	