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ANTIFREEZE LIQUIDS

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This invention relates to a polyhydric alcohol anti-freeze liquid of the type adapted to be added to water in the circulating cooling system of an internal combustion engine; and more particularly, the invention involves such an anti-freeze liquid having an improved combination of corrosion inhibitors.

The invention is applicable to the various types of water-miscible polyhydric alcohols employed as freezing point depressants for water in circulating cooling systems, such as ethylene and other glycols and polyglycols and glycerine. The preferred embodiment of the present invention employs ethylene glycol as the freezing point depressant. It is well recognized that, in service, such anti-freeze liquids give rise to rather serious corrosion of the metals, namely, steel, brass, copper, aluminum, solder and their alloys, with which they come in contact in the circulating system; and various corrosion inhibitors and inhibitor combinations have been employed in an effort to overcome that difficulty.

One of the principal objects of the present invention is to provide an anti-freeze liquid of this character containing a superior combination of corrosion inhibitors to effectvely protect the metal parts of the circulating system over long periods of service.

Another object of the present invention is to provide a glycol anti-freeze of the so-called permanent type which will retain inhibiting amounts of the superior anti-corrosive combination over long periods of service without replacement of the inhibitors.

Still another object of the invention is to provide an anti-freeze liquid which can be satisfactorily reinhibited after such lengthy service.

Another object of the invention is to provide an improved method of manufacturing such an anti-freeze liquid. Other objects and advantages of the invention will be apparent from the following description when taken in conjunction with the appended claims.

In accordance with the present invention, these objectives are attained by incorporating in the

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polyhydric alcohol anti-freeze liquid a combination of an alkali metal phosphate, an alkali metal silicate and mercaptobenzothiazole or an alkali metal salt of mercaptobenzothiazole. While both combinations of inhibitors specified above provide superior anti-corrosive properties over the inhibitors currently in use, and are included within the scope of this invention, it is to be understood that the combination including the alkali metal salt of mercaptobenzothiazole is preferred as having certain unexpected advantages in long time service over the combination containing mercaptobenzothiazole. While the various specified alkali metal salts, including those of sodium, potassium, etc., may be used, the sodium salt is preferred from the standpoint of availability and effectiveness. In the following description, the sodium salt will therefore be referred to; but it is to be understood that the corresponding salts of the other alkali metals may be substituted therefor.

The sodium phosphate employed is the trisodium phosphate. Ordinarily, the trisodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) is used. The sodium silicate, which is conveniently employed in the form of a concentrated aqueous solution, is preferably one having a high SiO_2 to Na_2O mol ratio in excess of 2.5:1, such as the well-known "N" brand of sodium silicate marketed by the Philadelphia Quartz Company having a SiO_2 to Na_2O mol ratio of about 3.2:1. The mercaptobenzothiazole can be employed in the form of a powder and dissolved in the glycol anti-freeze. However, the sodium mercaptobenzothiazole is preferably employed in the form of a concentrated aqueous solution of about 45–50% concentration, a commercial form of the material on the market being an aqueous solution containing about 46–47% by weight of sodium mercaptobenzothiazole.

Based on extensive laboratory and service tests, the proportions in which the various constituents of the inhibitor combination are employed are set forth in the following tabulation, together with a preferred example of each combination,

the percentages being expressed by weight based on ethylene glycol:

COMPOSITION A

	Limits Per Cent by Wgt.	Example Per Cent by Wgt.
$Na_3PO_4.12H_2O$	1.0–3.5	2.38
40° Bé. "N" Brand Sodium Silicate Solution	0.8–1.5	1.0
50% Aqueous Solution of Sodium Mercaptobenzothiazole	0.5–1.2	0.68

Or expressed on a water-free basis in per cent by weight based on ethylene glycol.

	Limits Per Cent by Wgt.	Example Per Cent by Wgt.
Na_3PO_4	0.4–1.6	1.03
Sodium Silicate	0.3–0.6	0.4
Sodium Mercaptobenzothiazole	0.25–0.6	0.34

COMPOSITION B

	Limits Per Cent by Wgt.	Example Per Cent by Wgt.
$Na_3PO_4.12H_2O$	1.0–3.5	2.5
40° Bé. "N" Brand Sodium Silicate Solution	0.8–1.5	1.0
Mercaptobenzothiazole	0.2–0.5	0.3

Or expressed on a water-free basis in percent by weight based on ethylene glycol

	Limits Per Cent by Wgt.	Example Per Cent by Wgt.
Na_3PO_4	0.4–1.6	1.08
Sodium Silicate	0.3–0.6	0.4
Mercaptobenzothiazole	0.2–0.5	0.3

The anti-freeze liquid containing either of the above combinations within the limit specified in a 40% concentration in water has a pH in excess of 9 and below 12, generally about 10.7–11.2. The reserve alkalinity of the anti-freeze liquid, and its ability to retain excess alkalinity over long periods of service, are valuable properties of the compositions of the present invention.

In manufacturing the anti-freeze liquid of Composition A above, the trisodium phosphate dodecahydrate is first dissolved at an elevated temperature of the order of 180–200° F. in a small amount of water. Then the sodium silicate and sodium mercaptobenzothiazole solutions are admixed therewith in the order mentioned. The amount of water employed, including the bound water of the trisodium phosphate dodecahydrate and the free water in the concentrated aqeous solutions of sodium silicate and sodium mercaptobenzothiazole, is preferably not substantially more than about the minimum required to maintain the said salts in solution at the elevated temperature, and thus provide a nearly saturated aqueous solution thereof at that temperature. A small flowing stream of the resulting aqueous solution, in controlled amount, is then admixed with a flowing stream of the alcoholic freezing point depressant, such as ethylene glycol, in controlled amount, to provide about 3–8% by weight of the former to about 97–92% by weight of the latter in the resultant mix. This provides an anti-freeze liquid containing roughly about 2–5% by weight of water based on the final anti-freeze liquid, and preferably about 3–4% total water. Actually, the amount of water initially added to dissolve the trisodium phosphate is much less than the figure specified above for total water, and represents about 1–2% by weight based on the final anti-freeze liquid. The small amount of water adds materially to the ease of preparation, and to the stability of the ultimate anti-freeze liquid on storage against sedimentation and salt separation and yet is so small as not to affect the normal freezing point depressant properties of the ultimate anti-freeze liquid as compared to substantially pure ethylene glycol or other freezing point depressant. In manufacturing the anti-freeze liquid of Composition B above, the procedure is essentially the same except that the mercaptobenzothiazole powder for convenience is separately dissolved in the glycol, preferably before mixing of the streams of aqueous solution and glycol.

It will be understood that the resulting anti-freeze liquid is ordinarily mixed with two and one half times its volume of water to form a 40% solution for use in the northern zones of most temperate climates, and with about four times its volume of water to form a 20% solution for use in the southern zones of such temperate climates; however, the anti-freeze liquid can, of course, be admixed in any proportion desired to provide the required freezing point according to freezing point tables, except that the glycol anti-freeze liquid should not be employed in a higher concentration in water than about 60%, because the more concentrated liquid becomes unduly viscous at extremely low temperatures. This is true of all glycol base anti-freeze liquids.

The following examples and tables are given to illustrate the unusual effectiveness of the compositions of the present invention.

EXAMPLE I

An anti-freeze liquid consisting of ethylene glycol had admixed therewith the following ingredients in per cent by weight based on the ethylene glycol:

	Per cent
$Na_3PO_4.12H_2O$	2.5
40° Bé. "N" brand sodium silicate solution (approximately 60% H_2O)	1.0
Mercaptobenzothiazole	0.3
Distilled water	3.0

The foregoing composition was compared as to anti-corrosive properties with two of the leading ethylene glycol anti-freeze compositions now on the market by a so-called accelerated corrosion test. In this test, cleaned and polished test strips having dimensions of ½" x 4" x 1/16" of aluminum, brass, copper and steel, together with a 4" length of ⅛" wire solder specimen are employed. These metals are representative of the types usually found in an automobile cooling system. The weighed specimens are immersed in 200 cc. of a 40% aqueous solution of the inhibited glycol confined within a pressure vessel at 212° F. under 100 pounds per sq. in. initial oxygen pressure for a predetermined length of time, usually about 24 hours or 60 hours. The test specimens are then removed, cleaned and reweighed to determine the weight loss in milligrams, and the appearance of the specimens and the test solution after the test is observed. The following results were obtained in this sixty hour accelerated corrosion test on the foregoing com-

position and two leading commercial compositions, all being tested in 40% aqueous solution:

Table I

	Composition Example I, Average of seven runs	Commercial Anti-Freeze No. 1, Average of two runs	Commercial Anti-Freeze No. 2, Average of two runs
Wgt. Loss of Specimen, mgs.			
Aluminum	5.7	185.2	28.8
Brass	5.3	29.4	13.8
Solder	5.1	20.8	81.9
Copper	10.4	30.4	10.7
Steel	4.8	6.6	10.8
Appearance of specimens at end of test.	Aluminum, brass, solder, and copper were clean; steel had small black spot.	Aluminum was pitted and covered with barnacles; brass and copper were tarnished; solder was light gray; steel was substantially clean.	Aluminum was light gray with deposit in local area; brass and copper were tarnished; solder was clean; steel was clean except in local area.

The foregoing tests show that the inhibitor composition of the present invention is unusually effective in repressing attack on all of the metals normally encountered in a circulating cooling system. It may be stated that this accelerated corrosion test has been found by long experience to be a rather rigorous laboratory test eminently suitable as a screening test to cull out inferior compositions, and to detect promising compositions which are then subjected to the laboratory simulated engine test as described later, and to practical service tests. However, the marked differences in corrosion protection evidenced by the foregoing results are conclusive of the exceptional superiority of the present composition, as has been proven by further comparative laboratory and practical service tests.

The following results were obtained in the said sixty hour accelerated corrosion test on the individual components of the foregoing inhibitor combination, together with a blank run (uninhibited ethylene glycol). All tests were again made in 40% aqueous solution.

Table II

Inhibitor	None	2.5% Trisodium Phosphate	1.0% Sodium Silicate	0.3% Mercaptobenzothiazole
Wgt. loss of specimen, mgs.				
Aluminum	35.3	48.3	13.8	25.1
Brass	25.5	3.8	16.4	18.4
Solder	30.8	62.8	7.5	6.4
Copper	13.0	24.8	13.1	19.5
Steel	230.8	0.7	371.6	248.7

It should be understood that, in the foregoing Table II, the percentage figures listed for trisodium phosphate and sodium silicate represent the trisodium phosphate dodecahydrate and the 40° Bé. "N" brand sodium silicate solution, respectively. The blank run of column 2 shows the typical corrosiveness of the uninhibited glycol to steel, aluminum, solder and brass. Column 3 shows that the primary effect of the trisodium phosphate is to protect steel and brass against this corrosion; but the presence of the phosphate then adds problems due to enhanced corrosion on other metals, particularly aluminum and solder. The fourth column shows that sodium silicate by itself reduces the corrosion on aluminum, brass and solder but greatly enhances the corrosion of steel. While mercaptobenzothiazole has been suggested as a corrosion inhibitor for copper containing metals, the fifth column shows that, when used alone, it has an apparently reverse effect on copper, and also slightly increases the corrosion of steel. By comparison with the data on the

combination of inhibitors of the present invention, as set forth in Table I, it is readily apparent that the three inhibitors have a true combination effect on all of the metals with the possible exception of steel, and the latter is effectively protected in the presence of the combination. The net result of the combination of inhibitors is to substantially reduce the average corrosion of all the metals over that heretofore attained by commercial anti-freeze liquids, and to provide a novel anti-freeze liquid which maintains its highly effective inhibiting action over long periods of service.

One important function of the mercaptobenzothiazole, or the alkali metal salt thereof, in the combination is to maintain the reserve alkalinity of the present anti-freeze liquid in service, although it may be mentioned that the mechanism of this action is not known. This is illustrated in the following table which shows the results obtained on analysis of the used glycol anti-freeze liquid when employed in 40% concentration in water in the described sixty hour accelerated corrosion test. In each case, the anti-freeze liquid was of the same composition as set forth above for Example I, except for variation in the percentage of mercaptobenzothiazole employed. The alkalinity of the glycol liquid was determined before and after the accelerated corrosion test by titration with 0.1 normal HCl, and the decrease in alkalinity set forth in the table represents the difference in the number of cc. of the 0.1 normal HCl required to neutralize 50 cc. of the anti-freeze solution to pH 7 before and after the test.

Table III

Per Cent Mercaptobenzothiazole	Decrease of Alkalinity
0	19.3
0.1	16.4
0.3	14.5
0.5	11.9

As a result of extended tests, it has been found that the high pH and also the high reserve alkalinity of the present anti-freeze liquid contributes materially to the unusual effectiveness thereof in inhibiting corrosion. The reserve alkalinity functions to react with acids formed through oxidation of the glycol. The foregoing Table II demonstrates that the mercaptobenzothiazole should be employed in a proportion based on the glycol of at least 0.2% and preferably about 0.3% or somewhat higher in order to preserve this reserve alkalinity over extended periods of service. The sodium mercaptobenzothiazole is even more effective in this respect, and the latter should be employed in a proportion of

at least about 0.25% and preferably about 0.34% or somewhat higher based on the glycol.

It has heretofore been suggested that an alkali metal phosphate be employed in combination with an alkali metal borate as a corrosion inhibiting combination for an alcoholic anti-freeze liquid, such as a glycol; and it was also suggested that a small proportion of the order of 0.05 to 0.10% by weight based on the glycol of mercaptobenzothiazole may be included for reinhibitor purposes.

In order to evaluate the effectiveness of the suggested borate-phosphate combination on a comparative basis with that of the present silicate-phosphate combination, an equal percentage of mercaptobenzothiazole within the higher proportion range (above 0.2% by weight based on the glycol) found effective in maintaining the reserve alkalinity of the present combination was used in the comparative tests. Sixty hour accelerated corrosion tests were thus run on the following compositions consisting of ethylene glycol containing the indicated percentages by weight of inhibitor ingredients and tested in 40% concentration in water, with the following pH values of each solution being obtained before and after the sixty hour test

Table IV

Composition of glycol solution, per cent by wt. basis glycol	1.0% $Na_2B_4O_7.10H_2O$ 2.5% $Na_3PO_4.12H_2O$ 0.3% Mercaptobenzothiazole 3.0% H_2O	1.0% Na silicate—40° Bé. "N" brand 2.5 $Na_3PO_4.12H_2O$ 0.3% Mercaptobenzothiazole 3.0% H_2O
pH of fresh 40% concentrate in H_2O	8.5	11.1
pH of used 40% solution	7.7	10.8

While the weight losses of the various metals in the above sixty hour accelerated corrosion tests for both solutions were small and substantially of the order shown in the left hand column of Table I above, thus indicating that the two compositions were essentially equal in corrosion inhibition for the limited time period of this test, the pH data is reproduced in Table IV as being of more significance. The relatively low initial pH of 8.5 of the borate combination, and the more rapid decline of its pH to 7.7 in the sixty hour test, shows that this anti-freeze liquid would fail to satisfy the requirements of a so-called permanent type of glycol anti-freeze of maintaining its effectiveness without reinhibition over many hundreds of hours under actual service conditions. On the other hand, the composition of the present invention with a relatively high initial pH of 11.1 and a relatively low rate of decline of only 0.3 over the sixty hour period shows that the mercaptobenzothiazole is far more effective in the silicate-phosphate combination in maintaining the required reserve alkalinity of the anti-freeze liquid over long periods of service. This has been proved by simulated service tests of long duration, as described hereinbelow. These tests have shown that, when the reserve alkalinity has been consumed, the corrosion inhibiting effect is lost, and corrosion of the various metals then proceeds at a rate which may even exceed that of an uninhibited glycol. It will be appreciated that the borate composition of the foregoing table contains three times the maximum amount of mercaptobenzothiazole suggested by the prior art; and the combination of the prior art is even less effective as a permanent type glycol anti-freeze.

EXAMPLE II

The foregoing data under Example I show that the inhibitor combination containing mercaptobenzothiazole is highly effective for purposes of the present invention. The following data illustrate the unexpected superiority of the combination containing the sodium salt of mercaptobenzothiazole over that containing mercaptobenzothiazole. Two compositions containing sodium mercaptobenzothiazole were employed in these tests, the compositions differing only slightly in the percentages of trisodium phosphate and water as follows:

Composition of Solution, Per Cent by weight basis glycol	Composition 2	Composition 3
	Per Cent	*Per Cent*
$Na_3PO_4.12H_2O$	2.5	2.38
40° Bé. "N" Brand Sodium Silicate Solution	1.0	1.0
50% Aqueous Solution of Sodium Mercaptobenzothiazole	0.68	0.68
Distilled Water	1.23	1.52

One practical advantage for use of sodium mercaptobenzothiazole is that it is soluble in water and can be employed in a concentrated aqueous solution; whereas mercaptobenzothiazole is insoluble in water and adds a manufacturing problem when it is separately dissolved in the glycol. But, of more importance, is the fact that sodium mercaptobenzothiazole possesses unexpected properties in retarding the consumption of the ingredients of the inhibitor combination in service, gives superior results, particularly from the standpoint of protection for steel, when a used glycol solution is reinhibited, and finally provides superior results from the standpoint of overall corrosion inhibition in so-called permanent type service of long duration.

The following results were obtained in a so-called simulated engine test on Composition No. 3 immediately above in comparison with the composition of Example I containing mercaptobenzothiazole.

In this simulated engine test, the test unit consists of a circulating cooling system having an automotive water pump forcing the 40% aqueous solution of the anti-freeze in series through a test reservoir, then in parallel through two radiators from automobile heaters, and the combined streams from the radiators then are forced past an electric heater and return to the suction side of the pump. The anti-freeze solution is maintained at 200° F. by means of an automatic temperature controller connected to the electric heater, this being somewhat above the normal running temperature in automotive cooling systems, and being selected to make the test more rigorous. A small stream of air (20 cc. per minute) is bled into the system at the suction connection of the water pump to supply

oxygen necessary for corrosion and to accelerate oxidation of the anti-freeze to corrosive acids. Polished and weighed metal specimens similar to those described above in connection with the accelerated corrosion test are suspended in the circulating anti-freeze in the test reservoir. The effectiveness of the corrosion inhibition is judged by the weight loss and appearance of the test specimens after several hundred hours operation, such as after 300 hours and 600 hours. This test thus simulates the actual service conditions of the anti-freeze in use in the circulating cooling system of an internal combustion engine.

The following Table V sets forth data obtained in this simulated engine test in comparative runs on the composition of Example I with Composition 3 above, both compositions being tested in 40% concentration:

Table V

Anti-Freeze Combination	Composition—Example I	Composition 3
Average weight loss of specimens in 300 hrs. operation, mg.		
Aluminum	16.9	3.8
Brass	19.1	11.0
Solder	12.8	9.9
Copper	20.9	13.2
Steel	9.1	8.2
Number of runs included in average	9	6
Average weight loss of specimens in 600 hrs. operation, mg.		
Aluminum	61.8	4.0
Brass	20.0	16.8
Solder	28.6	16.0
Copper	26.9	19.9
Steel	14.4	9.4
Number of runs included in average	4	4

The foregoing data show the composition containing sodium mercaptobenzothiazole to be uniformly more effective in inhibiting corrosion over long periods of service on all of the metals, and particularly on aluminum, than the composition containing mercaptobenzothiazole. The latter, however, is highly effective, since the weight loss figures are low for this rigorous test of long duration; and the results for Composition 3 are therefore unusually outstanding.

Chemical analyses of the anti-freeze solutions before and after the simulated engine tests have also shown that the sodium mercaptobenzothiazole is superior to the mercaptobenzothiazole in this combination in its retarding effect on the consumption of the inhibitor ingredients. An example of typical data of this character which have been obtained is set forth in the following Table VI, the analyses being made on the anti-freeze liquids of Example I and Composition 2 before and after the indicated hours of operation in the above described simulated engine test:

Table VI

Anti-Freeze Combination	Composition—Example I		Composition 2	
Hrs. Operation	0	300	0	959
Concentration of Inhibitors, wgt. per cent				
Phosphate as P_2O_5	0.18	0.08	0.17	0.16
Silicate as SiO_2	0.11	0.02	0.11	0.03
Mercaptobenzothiazole	0.11	0.005	0.11	0.04

The foregoing table shows that the sodium mercaptobenzothiazole, in a service test of more than three times the duration of that employed on the composition containing mercaptobenzothiazole, gave uniformly better conservation of the three inhibitors in the combination, and particularly conserved the trisodium phosphate which is instrumental in preserving the reserve alkalinity and the effectiveness of the solution as an anti-corrosive.

This is further illustrated by the relative rates of decrease of the pH and reserve alkalinity, wherein the following values set forth in Table VII were obtained in the above simulated service test runs of Table VI:

Table VII

Hours Operation	Composition—Example I		Composition 2	
	pH	Alkalinity	pH	Alkalinity
Initial	11.1	23.5	10.8	24.3
100	8.4	3.7		
200	7.9	3.0	9.7	10.2
300	7.1	0.5		
400			9.2	7.2
600			8.1	4.6
700			7.8	5.4

In the above Table VII, alkalinity means the number of cc. of 0.1 normal HCl required to neutralize 50 cc. of the solution to pH 7.0. As shown, the sodium mercaptobenzothiazole gave unexpectedly superior results over the mercaptobenzothiazole in maintaining the pH and reserve alkalinity of the anti-freeze liquid for a considerably longer period in the simulated service test.

It is desirable that an anti-freeze liquid be capable of being reinhibited by the addition of a concentrate of the inhibitor combination after a long period of service. This is not uniformly successful, however, since many inhibitor combinations which provide fairly satisfactory corrosion resistance on initial use fail to provide the required degree of protection when added for reinhibiting purposes to a used anti-freeze liquid. For purposes of reinhibition, the present composition containing the sodium mercaptobenzothiazole is unexpectedly superior to the composition containing mercaptobenzothiazole, as illustrated by the following Table VIII. This sets forth data obtained in simulated engine tests on several samples of used anti-freeze liquid of the composition of Example I when reinhibited, the average weight losses being reported, in comparison with the data obtained on the reinhibited anti-freeze liquid of Composition 2.

Table VIII

Reinhibited Antifreeze Combination	Composition Example I	Composition 2
Hrs. Operation	300	300
Average wgt. loss of specimens, mg.		
Aluminum	13.3	1.3
Brass	11.4	12.6
Solder	7.3	10.4
Copper	16.1	13.0
Steel	31.5	5.9
Number of runs included in average	2	2

The foregoing table shows that the reinhibited anti-freeze liquid containing the sodium mercaptobenzothiazole retains its effectiveness on all of the metals, while the reinhibited composition containing mercaptobenzothiazole has lost some of its anti-corrosive effectiveness on steel.

EXAMPLE III

The following illustrates the method of manufacturing 520 barrels (42 gallons per barrel) of finished anti-freeze of Composition 3 above, by blending 500 barrels of ethylene glycol (20,830 gallons measured at 60° F.) with the following quantities of inhibitor ingredients:

Inhibitor	Wgt. in lbs.	Per Cent by Wgt.
Trisodium phosphate dodecahydrate	4,610	42.5
40° Bé. "N" Brand sodium silicate solution (Philadelphia Quartz Co.)	1,940	17.9
47% aqueous solution of sodium mercaptobenzothiazole	1,320	12.2
Water	2,960 (355 gals.)	27.3
Dye	10–25	0.1–0.2

The finished anti-freeze liquid is prepared by blending the following amounts of ethylene glycol with the above listed inhibitor combination.

Finished Anti-Freeze	Wgt. in lbs.	Per Cent by Wgt.
Ethylene Glycol	193,800	94.7
Inhibitor	10,842	5.3

In preparing the anti-freeze liquid, the 355 gallons of deionized water, such as boiler feed water or suitable natural water having low calcium, magnesium, iron, chloride, and sulfate content, were pumped into a tank equipped with a mixer and a steam jacket. The temperature of the water was raised to 180–200° F. by introducing steam into the jacket while operating the mixer. The indicated quantity of a water soluble and glycol soluble dye was added, and the contents were agitated at the elevated temperature for a half hour. The indicated quantity of trisodium phosphate dodecahydrate was then added gradually over a period of approximately two hours while agitating and maintaining the water temperature at 180–200° F., and the contents were then mixed another half hour at this temperature to complete solution of the phosphate. The indicated quantity of the sodium silicate solution was then added over a period of about one-half hour, followed by addition of the aqueous solution of the sodium mercaptobenzothiazole over a period of about twenty minutes, both under the same conditions of agitation and temperature. Then a stream of the inhibitor solution at the elevated temperature was pumped from the tank at a controlled rate and mixed with a much larger stream of ethylene glycol being pumped from a storage tank held at atmospheric temperature, the mixed streams passing to a large blending tank equipped with an agitator. The pumping and mixing of the streams required about one and one-half hours to complete, and the contents of the large blending tank were then agitated at atmospheric temperature for an additional four hours. The anti-freeze liquid was then in condition for filling into cans or other containers at the packaging plant.

Typical tests obtained on the finished anti-freeze liquid are as follows:

Specific gravity at 60°/60° F	1.1288
pH	10.73
Alkalinity—cc. of 0.1 normal HCl required to titrate 25 cc. sample to pH 7.0	36
Phosphorus calculated as per cent P_2O_5	0.42
Silicate calculated as per cent SiO_2	0.28
Sodium mercaptobenzothiazole, per cent	0.32
Water, per cent	3.7

Obviously many modifications and variations of the invention as above set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. An anti-freeze liquid adapted to be added to water for circulating cooling systems containing metallic parts normally subject to corrosion consisting essentially of a water-miscible polyhydric alcohol freezing point depressant, water, and a corrosion inhibitor combination consisting in percentage by weight based on the polyhydric alcohol of 0.4–1.6% of a trialkali metal phosphate, 0.3–0.6% of an alkali metal silicate, and 0.2–0.6% of a compound selected from the group consisting of mercaptobenzothiazole and an alkali metal salt of mercaptobenzothiazole.

2. An anti-freeze liquid, according to claim 1, wherein the tri-alkali metal phosphate is trisodium phosphate, the alkali metal silicate is sodium silicate having a SiO_2 to Na_2O mol ratio in excess of about 2.5:1, and the said compound is sodium mercaptobenzothiazole, said liquid in 40% concentration in water having a pH in excess of 9 and below 12.

3. An anti-freeze liquid consisting essentially of ethylene glycol, water, and a corrosion inhibitor combination consisting in percentage by weight based on the ethylene glycol of 0.4–1.6% of Na_3PO_4, 0.3–0.6% of sodium silicate having an SiO_2 to Na_2O mol ratio of 3.1:1 to 3.3:1, and 0.25–0.6% of sodium mercaptobenzothiazole.

4. An anti-freeze liquid consisting essentially of about 94.7% by weight of ethylene glycol and about 5.3% by weight of an inhibitor combination consisting essentially of the following ingredients in about the following percentages by weight:

	Per cent
Water	27.3
Trisodium phosphate dodecahydrate	42.5
40° Bé. aqueous solution of sodium silicate having an SiO_2 to Na_2O mol ratio of about 3.2:1	17.9
45–50% aqueous solution of sodium mercaptobenzothiazole	12.2
Dye	0.1

5. The method of forming an anti-freeze liquid which comprises dissolving at elevated temperature of the order of 180–200° F. in not substantially more than the minimum amount of water which will maintain the following anti-corrosive ingredients in solution at the said elevated temperature to form a nearly saturated solution, a tri-alkali metal phosphate, an alkali metal silicate and an alkali metal salt of mercaptobenzothiazole, and then admixing with agitation a stream of the resulting aqueous solution at the said elevated temperature with a stream of a water-soluble polyhydric alcohol pour depressant, said streams being added in controlled proportions to provide about 3–8% by weight of the aqueous solution to about 97–92% by weight of the water-soluble polyhydric alcohol and thereby produce the anti-freeze liquid containing in percentage by weight based on the polyhydric alcohol about 0.4–1.6%

of the tri-alkali metal phosphate, 0.3–0.6% of the alkali metal silicate and 0.2–0.6% of the alkali metal salt of mercaptobenzothiazole, said anti-freeze liquid containing about 2–5% by weight of water based on the anti-freeze liquid.

6. The method of forming an auti-freeze liquid which comprises dissolving in water at an elevated temperature of about 180–200° F. and in order as listed hereinafter trisodium phosphate dodecahydrate, a concentrated aqueous solution of sodium silicate, having an SiO_2 to Na_2O mol ratio of about 3.1:1 to 3.3:1, and a concentrated aqueous solution of sodium mercaptobenzothiazole, the amount of water used being not substantially more than about the minimum to maintain the said salts in solution at the said elevated temperature and provide a nearly saturated solution thereof, and then admixing with agitation a flowing stream of the said aqueous solution at the said elevated temperature and in controlled amount with a flowing stream of ethylene glycol in controlled amount to provide about 3–8% by weight of the former to about 97–92% by weight of the latter and thereby produce the anti-freeze liquid containing in percentage by weight based on the ethylene glycol about 0.4–1.6% of trisodium phosphate, 0.3–0.6% of sodium silicate and 0.2–0.6% of sodium mercaptobenzothiazole, said anti-freeze liquid containing about 2–5% by weight of water based on the anti-freeze liquid.

WILLIAM R. SMITH.

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