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3,445,395

COMPOSITION OF IMPROVED WATER-GLYCOL ANTIFREEZE AND HEAT EXCHANGE MEDIA AND PROCESS FOR MANUFACTURE OF SAME

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No Drawing. Continuation-in-part of application Ser. No. 452,354, Apr. 30, 1965. This application Oct. 12, 1967, Ser. No. 674,715

Int. Cl. C09k 3/02

U.S. Cl. 252-75

6 Claims

ABSTRACT OF THE DISCLOSURE

A liquid composition suitable for use in aqueous liquid heat exchange-type cooling systems for internal combustion engines consisting essentially of about 90 to 96 weight percent dihydroxyaliphatic alkanol having about 2 to 6 carbon atoms, about 0.5 to 3.0 weight percent alkali metal orthophosphate, about 0.1 to 3.0 weight percent alkali metal borate, about 0.1 to 1.0 weight percent mercaptobenzothiazole compound, and about 0.05 to 0.5 weight percent water-soluble complex phosphate depicted by the general formula, $A_xZ_yP_wO_v$, wherein A is alkali metal, Z is selected from the group consisting of zinc and magnesium, P is phosphorous, O is oxygen, x is about 2 to 3.8, y is about 0.1 to 1.0, the ratio x/y is about 2 to 3.8, v is about 7 to 10, w is about 2 to 3 and the ratio v/w is about 3.3 to 3.8, and sufficient minor amount of water necessary to effectively dissolve the components.

This application is a continuation-in-part of copending U.S. patent application Ser. No. 452,354, filed Apr. 30, 1965.

This invention relates to alcoholic antifreeze compositions suitable for use in aqueous liquid heat exchange cooling systems and, more particularly, for internal combustion engine cooling systems.

As is well known to those skilled in the art, glycol-based antifreeze compositions for use in heat exchange systems, and particularly automotive cooling systems, possess definite advantages as compared with volatile antifreeze compositions employing lower aliphatic alcohols. However, these glycol-based antifreeze compositions require compounding with corrosion inhibitors, antifoam additives, and other compatible additives to prevent the corrosion of metals and the foaming of the solution obtained by diluting the antifreeze with various potable waters. It is well known that the metal parts in the cooling systems of internal combustion engines often comprise iron, copper, brass, solder, steel and aluminum. Due to the variety of metals used and varied resulting metal combinations, the long-term prevention of corrosion on all metals is particularly difficult because of galvanic cells, additive interaction and depletion.

The prior art has suggested the use of many types of corrosion inhibitors among which may be mentioned borax, arsenites, triethanolamine, sulfonated oils, resins, sodium nitrite, sodium benzoate, triethanol ammonium phosphate, mercaptobenzothiazole and alkali metal mercaptobenzothiazole, maleic acid, picric acid, bolybdates, tungstates, urea, naphthenates, etc., which are used either alone or in combinations.

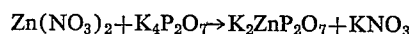
The inhibitors, known up to now, differ to a rather considerable degree as to their effect in connection with various metallic materials. Thus, there are known inhibitors which give a maximum effect in connection with light metals (for example, in cylinder heads) while others are more suited for nonferrous, heavy metals such as

copper, and their alloys (for example, in heat exchanger constructions), and again others are relatively well suited for ferrous metal castings (for example, in motor blocks). It it, therefore, a problem to find an inhibitor or combination thereof which gives the greatest possible protective effect for the combinations of iron-like metals, light metals such as aluminum, heavy non-ferrous metals such as copper and alloys of such metals. While the inhibitors discussed above are suitable for many uses, they present serious problems where high speed, that is, high r.p.m. aluminum alloy cooling fluid pumps are employed. It has been found that where high r.p.m. aluminum alloy cooling liquid pumps are employed in the system that, in general, the antifreeze compositions employing the above inhibitors do not meet the performance requirements of the automobile industry.

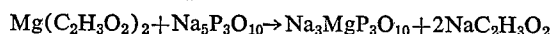
Accordingly, it is a purpose of this invention to provide a liquid antifreeze composition which is suitable for use in aqueous liquid heat exchange-type cooling systems for internal combustion engines wherein said aqueous liquid is circulated by a high r.p.m. aluminum alloy pump and which composition is not detrimental to other parts of the conventional cooling system.

The foregoing and other objects of the invention are achieved by a liquid composition suitable for mixing with water which includes about 90 to 96 weight percent dihydroxy aliphatic alcohol having about 2 to 6 carbon atoms, about 0.5 to 3.0 weight percent alkali metal orthophosphate, about 0.1 to 3.0 weight percent alkali metal borate, about 0.1 to 1.0 weight percent of mercaptobenzothiazole compound, about 0.05 to 0.5 weight percent water-soluble complex phosphate depicted by the following general formula, $A_xZ_yP_wO_v$, wherein A is alkali metal, Z is selected from the group consisting of zinc and magnesium, P is phosphorous, O is oxygen, x is about 2 to 3.8, y is about 0.1 to 1.0, the ratio x/y is about 2 to 3.8, v is about 7 to 10, w is about 2 to 3 and the ratio v/w is about 3.3 to 3.8, and sufficient minor amount of water necessary to efficiently dissolve the additives.

The composition of this invention is preferably prepared by preparing a solution of a zinc or magnesium compound, or both, and alkali metal pyrophosphates or polyphosphates, or both, and a solution of the remaining components and then combining the two solutions. The zinc and/or magnesium compounds react with the pyrophosphate and/or polyphosphate to produce the compound having the formula, $A_xZ_yP_wO_v$, set forth above. More specifically, by way of illustration, when the zinc compound is zinc nitrate and the pyro- or polyphosphate is potassium pyrophosphate, the reaction is as follows:



Similarly, if the magnesium compound is magnesium acetate and sodium polyphosphate is employed, the following reaction takes place:



When the antifreeze composition is diluted with water, a clear solution is formed, proving that the insoluble compounds $Zn_2P_2O_7$ and $Mg_2P_2O_7$ have not been formed, and that the complex phosphates as shown in the above formulas have been formed. In the ultimate aqueous solution the complex phosphate, e.g., $K_2ZnP_2O_7$, may ionize in the following manner:



As a source of magnesium or zinc, a wide variety of compounds obvious to those skilled in the art may be employed, such as, for example, zinc nitrate, zinc acetate, zinc trimethylolphenate, zinc thiosulphate, zinc oxide, zinc fluoride, zinc iodate, zinc salicylate, magnesium acetate, magnesium arsenite, magnesium ferrocyanide, mag-

nesium fluosilicate, magnesium nitrate, magnesium oxide, magnesium sulphate, and magnesium thiosulphate. The alkali metal pyrophosphates and polyphosphates which may be employed preferably have mole ratios of oxygen to phosphorous of about 3.3 to 3.8. These include sodium and potassium pyrophosphate, sodium and potassium hexametaphosphate and sodium and potassium tripolyphosphate.

The expressions "dihydroxyaliphatic alcohol," "alkali metal orthophosphate," "alkali metal borate" and "mercaptobenzothiazole compound" as used herein include mixtures of one or more members of the class defined by the expressions.

It has been found in accordance with this invention that the compound having the general formula, $A_xZ_yP_wO_v$, provides improved corrosion protection for aluminum and at the same time functions as an antifoam additive. The combination of orthophosphates and borates employed in the composition provides desirable corrosion protection for many metals and controls or buffers the pH in the range of 8 to 9 which is desirable for long-term use in cooling systems. Conventional alkaline agents such as alkali metal hydroxides may also be included to maintain the pH in the range of 8 to 9. The mercaptobenzothiazole compound provides good protection for corrosion of copper and brass surfaces and, in addition, acts as a moderate antioxidant for the glycols. The combination of zinc or magnesium ions in a solution with the orthophosphate, borate and mercaptobenzothiazole inhibitors provides a highly desirable combination of results and is particularly advantageous for use where aluminum pumps are employed in the cooling system. However, it was not possible to use such a composition in the prior art since the zinc or magnesium ions normally react with the orthophosphate, borate or the mercaptobenzothiazole inhibitors to give an undesirable product.

The applicant has discovered that by including in the composition a phosphate having the general formula $A_xZ_yP_wO_v$, set forth above, this problem is not presented.

It is desirable for the liquid composition of this invention to include at least one of the conventional antifoaming agents, such as nonionic surface active agents,

clude mono-, di- and tripotassium orthophosphate and mono-, di- and trisodium orthophosphate.

The mercaptobenzothiazole compounds which may be employed include 2-mercaptobenzothiazole and alkali metal mercaptobenzothiazoles such as sodium and potassium mercaptobenzothiazole.

It should be pointed out that the compositions discussed above are concentrates and in practice are added to water in a cooling system in a quantity sufficient to lower the freezing point of the final solution to the desired temperature. Thus, the amount of concentrate contained in the final coolant solution depends on the desired freezing point. In practice such final coolant solutions comprise about 15 to 60 weight percent of the above described concentrate, balance water. Thus, the final solution would consist essentially of about 15 to 60 weight percent dihydroxy aliphatic alcohol, about 0.15 to 1.8 weight percent alkali metal orthophosphate, about 0.05 to 1.8 weight percent alkali metal borate, about 0.01 to 0.6 weight percent of mercaptobenzothiazole compound, about 0.007 to 0.3 weight percent of a phosphate depicted by the formula, $A_xZ_yP_wO_v$, wherein A is alkali metal, Z is selected from the group consisting of zinc and magnesium, P is phosphorous, O is oxygen, x is about 2 to 3.8, y is about 0.1 to 1.0, the ratio x/y is about 2 to 3.8, w is about 7 to 10, v is about 2 to 3, the ratio v/w is about 3.3 to 3.8, and about 40 to 85 weight percent water. In addition, the final solution may contain about 0.001 to 0.1 weight percent antifoaming agent.

Illustrative examples of the antifreeze composition of this invention are shown in Table I below. An amount of conventional dye is added to each solution in amount to impart the desired color. The compositions of these examples are obtained by preparing a separate solution of the zinc nitrate, magnesium acetate and the pyrophosphate or polyphosphate in an amount of water of about 0.25 percent by weight of the final solution, whereby a phosphate depicted by the formula, $A_xZ_yP_wO_v$, described above, is obtained. A solution of the remaining components is prepared and these solutions are then combined. These solutions can be used as a stock solution for addition to water to provide the ultimate cooling fluid.

TABLE I

	Percent by weight										
	1	2	3	4	5	6	7	8	9	10	11
Ethylene glycol.....	80.21	80.21	95.0			95.0	95.0	85.0	85.0	80.21	80.21
Diethylene glycol.....	5.0	5.0		95.0				5.0	5.0	5.0	5.0
Propylene glycol.....	10.0	10.0			92.0			5.0	5.0	10.0	10.0
Dipotassium phosphate.....	1.56	1.56	1.0	2.0	2.5			1.5	1.5	1.56	1.56
Trisodium phosphate.....						1.0	3.0				
Sodium hydroxide, 50% aqueous.....	0.18	0.18	0.04	0.05	0.10					0.18	0.18
2-mercaptobenzothiazole.....	0.25	0.25	0.05	0.1	0.25	0.25	0.25	0.1	0.1		
Sodium mercaptobenzothiazole.....										0.25	
Potassium mercaptobenzothiazole.....											0.25
Sodium tetraborate-5-hydrate.....	0.36	0.36	0.5	1	2	0.5	0.5			0.36	0.36
Sodium metaborate-8-hydrate.....								0.5	0.5		
Tetrapotassium pyrophosphate.....	0.10	0.12	0.4	0.3	0.2	0.15	0.15			0.10	0.12
Sodium tripolyphosphate.....								0.3	0.3		
Zinc nitrate-6-hydrate.....	0.012	0.045				0.05	0.05	0.03		0.012	0.045
Magnesium acetate-4-hydrate.....	0.023		0.14	0.11	0.09					0.023	
Antifoam ¹	0.02	0.02	0.1	0.1	0.05	0.05	0.05	0.1	0.1	0.02	0.02
Water.....	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)

¹ The antifoam is the polyoxyethylene adduct of a polyoxypropylene hydrophobic base, having an average molecular weight of about 2,500, wherein the oxyethylene content is about 10 weight percent of the molecule.

² Balance.

silicone antifoam agents, aliphatic alcohols of 10 carbons or more, organic phosphates and phthalates.

The range of proportions for the antifoaming agent may vary widely. Good results are obtained with a coolant fluid containing as additive to the above described fluid base composition by weight of the overall composition, about 0.001 to 0.2 percent antifoaming agent.

The water-soluble dihydroxy aliphatic alcohols having 2 to 6 carbon atoms, which may be employed, include ethylene glycol, diethylene glycol, propylene glycol, and other alkylene glycols generally of the 1-2 series. The alkali metaorthophosphates, which may be employed, in-

The above antifreeze solutions exhibit a specific gravity 25/25° C. of about 1.15, a pH of about 8.5 for the formulations shown above and pH of about 8-9 when diluted with water to form a 50% by volume aqueous solution. Reserve alkalinity for 10 mls. is about 15 to 25. The freezing point of a 50% by volume aqueous solution is about -35° F. The equilibrium boiling point is about 340° F.

The superiority of the antifreeze composition of this invention over prior art commercial compositions is shown by the results of parallel tests which were run using antifreeze compositions of Examples 1 and 2 of Table I above,

in comparison with commercial antifreeze compositions containing well known prior art inhibiting agents and the compositions of Table II below.

TABLE II.—COMPOSITIONS, WEIGHT PERCENT

	1	2	3
Ethylene glycol.....	80.21	80.21	96.48
Diethylene glycol.....	5.0	5.0	-----
Propylene glycol.....	10.0	10.0	-----
Dipotassium phosphate.....	1.56	1.56	-----
Sodium hydroxide, 50% aqueous.....	0.18	0.18	-----
2-mercaptobenzothiazole.....	0.25	0.25	0.39
Sodium tetraborate-5-hydrate.....	0.36	0.36	-----
Zinc nitrate hexahydrate.....	0.012	0.045	-----
Magnesium acetate-4-hydrate.....	0.023	(²)	-----
Antifoam (same as Table I).....	0.02	0.02	-----
Water.....	(¹)	(¹)	1.87
Magnesium tetraborate.....	-----	-----	1.26

¹ Balance.

² Omit.

Compositions 1 and 2 set forth in Table II above were obtained by preparing a separate solution of the zinc nitrate and magnesium acetate in an amount of water of about 0.25% by weight of the final solution and a solution of the remaining components was prepared followed by a combination of the two solutions.

Compositions 1 and 2 above are identical respectively to the compositions of Examples 1 and 2 of Table I above, except that the complex phosphate was excluded to demonstrate the functionality of this component of the invention. In Table II, composition No. 3 is the composition of U.S. 3,015,629 to Truitt, and is exemplary of prior art patents on corrosion inhibited antifreeze compositions.

Table IV below sets forth test results for corrosion of various metals and the cavitation and erosion of aluminum circulation pumps used in internal combustion engine systems, with solutions of Detroit city water containing 15% by weight of the formulations of this invention as well as five commercial inhibited antifreeze compositions and compositions 1-3 of Table II above. In addition, results obtained with solutions of Examples 1 and 2 in ASTM 1384-61T, corrosive water, are also shown.

TABLE IV.—15% ANTIFREEZE IN DETROIT CITY WATER

Description	Pump cavitation and erosion rating		Corrosion losses in milligrams per square inch					
	Pump	Cover	Copper	Solder	Brass	Steel	Cast iron	Alu- minum
Commercial Antifreeze A-----	5	6	36	25	5	0	0	6
Commercial Antifreeze B-----	8	8	1	11	1	0	0	54
Commercial Antifreeze C-----	3	4	2	27	1	0	0	89
Commercial Antifreeze D-----	3	4	54	29	3	0	0	17
Commercial Antifreeze E-----	3	5	10	13	4	1	1	16
Composition 1 (Table II)-----	5	8	1	10	1.5	0.5	1	17
Composition 2 (Table II)-----	8	8	1	7	1	1	1	10
Composition 3 (Table II)-----	10	10	1	1	1	1	1	10
Ex. 1 (Table I) composition-----	10	10	0	2	1	0	0	1
Ex. 2 (Table I) composition-----	10	10	0	6	1	0	1	2
Antifreezes Diluted with ASTM 1384-61-T Corrosive Water								
Ex. 2 (Table I) composition at 50% conc. in water con- taining 100 p.p.m. ea. of chloride, sulfate, and bicarbonate-----	10	10	1	0	2	0	0	2
Ex. 2 (Table I) composition at 15% conc. in water con- taining 100 p.p.m. ea. of chloride, sulfate, and bicarbonate-----	9	10	0	8	1	1	3	3

The apparatus for the test consists of a standard automotive aluminum water pump having a capacity of 56 gallons per minute which rotates at a speed of 5000 r.p.m. and a cast metal reservoir about 10 inches in diameter by 12 inches high. The discharge and suction of the pump are connected by a circulation conduit of brass tubing and fittings and rubber hose whereby the antifreeze solution may be circulated from the discharge of the pump through the circulation conduit, the reservoir and back to the suction of the pump. A restrictive 3/4 inch diameter orifice is installed at the pump inlet. An adjustable flow control valve is placed between the pump discharge and the reser-

voir and is adjusted to give 16 to 22 inches of mercury vacuum at the pump inlet. The pump discharge pressure is controlled at 25 pounds per square inch gauge. This set of test conditions results in severe cavitation conditions within the aluminum pump. ASTM 1384-61-T metal corrosion specimens are mounted in the reservoir and weight losses for these metal specimens were determined by the ASTM 1384-61-T method and the results are shown in Table III below. A thermostatically controlled electric resistance heater is provided in the conduit to heat and maintain the temperature of the solution. At the start-up of the test the solution is maintained at about 110° F. After circulation has begun and the conditions level off, the coolant temperature is increased to 245° F. The pump is then operated for 100 hours under these conditions. The cover of the pump is removed at the completion of 100 hours and the effect of the coolant on the pump is determined by observing the condition, including pitting, etc., of the pump and cover thereof. The solution is then rated from 1 to 10 for pump cavitation and erosion as shown in Table III below.

TABLE III

	Rating
No erosion present; no metal loss	10
Very, very light, slight smoothing or shining of pump surface	9
Very light, slight roughness similar to sand cast aluminum surface	8
Light, medium roughness over 10-15% of area—random pitting	7
Medium-light, roughness over 25% of area, some very small pits or grooves	6
Medium, very rough (over 50% of area) some pits or grooves	5
Medium-severe, pits or grooves	4
Severe, large and deep pits or grooves, no failure	3
Very severe, very large or deep pits or grooves	2
Pump case leaking due to erosion	1

While there has been shown and described hereinabove the present preferred embodiments of this invention, it is to be understood that various changes, alterations, and modifications can be made thereto without departing from the spirit and scope thereof as defined in the appended claims.

What is claimed is:

1. A liquid composition suitable for use in aqueous liquid heat exchange-type cooling systems for internal combustion engines consisting essentially of about 90 to 96 weight percent dihydroxyaliphatic alkanol selected from the group consisting of ethylene glycol, diethylene

glycol, propylene glycol and mixtures thereof, about 0.5 to 3.0 weight percent alkali metal orthophosphate, about 0.1 to 3.0 weight percent alkali metal borate, about 0.1 to 1.0 weight percent of a compound selected from the group consisting of mercaptobenzothiazole and alkali metal mercaptobenzothiazoles, and about 0.05 to 0.5 weight percent water-soluble complex phosphate depicted by the general formula: $A_xZ_yP_wO_v$, wherein A is alkali metal, Z is selected from the group consisting of zinc and magnesium, P is phosphorous, O is oxygen, x is about 2 to 3.8, y is about 0.1 to 1.0, the ratio x/y is about 2 to 3.8, v is about 7 to 10, w is about 2 to 3 and the ratio v/w is about 3.3 to 3.8, and sufficient minor amount of water necessary to effectively dissolve the components.

2. The composition of claim 1 wherein said alkali metal borate is the tetraborate of a metal selected from the group consisting of sodium and potassium.

3. The composition of claim 1 which includes about 0.001 to 0.2 weight percent antifoaming agent selected from the group consisting of nonionic surface active agents, silicone antifoam agents, aliphatic alcohols of 10 carbons or more, organic phosphates and phthalates.

4. A liquid composition suitable for use in aqueous liquid heat exchange-type cooling systems for internal combustion engines consisting essentially of about 90 to 96 weight percent dihydroxyaliphatic alcohol selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol and mixtures thereof, from about 0.5 to 3.0 weight percent alkali metal orthophosphate selected from the group consisting of monopotassium phosphate, dipotassium phosphate, tripotassium phosphate, monosodium phosphate, disodium phosphate, trisodium phosphate and mixtures thereof, about 0.1 to 3.0 weight percent alkali metal borate, about 0.1 to 1.0 weight percent of a compound selected from the group consisting of mercaptobenzothiazole, sodium mercaptobenzothiazole and potassium mercaptobenzothiazole, about 0.05 to 0.5 weight percent of a water-soluble complex phosphate obtained by mixing in aqueous solution a phosphate selected from the group consisting of alkali metal pyrophosphates, alkali metal polyphosphates and mixtures thereof with about 0.001 to 0.10 weight percent of cations obtained by the inclusion in the composition of compounds selected from the group consisting of zinc nitrate, zinc acetate, zinc trimethylolphenate, zinc thiosulfate, zinc oxide, zinc fluoride, zinc iodate, zinc salicylate, magnesium acetate, magnesium arsenite, magnesium ferrocyanide, magnesium fluosilicate, magnesium nitrate, mag-

nesium oxide, magnesium sulfate and magnesium thiosulfate, and about 0.5 to 5 weight percent water.

5. An aqueous coolant fluid for use in heat exchange-type cooling systems for internal combustion engine consisting essentially of about 15 to 60 weight percent dihydroxyaliphatic alkanol selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol and mixtures thereof, about 0.15 to 1.8 weight percent alkali metal orthophosphate selected from the group consisting of monopotassium phosphate, dipotassium phosphate, tripotassium phosphate, monosodium phosphate, disodium phosphate, trisodium phosphate and mixtures thereof, about 0.05 to 1.8 weight percent of alkali metal borate, about 0.01 to 0.6 weight percent of a compound selected from the group consisting of mercaptobenzothiazole and alkali metal mercaptobenzothiazoles, about 0.007 to 0.3 weight percent of a water-soluble complex phosphate depicted by the following formula: $A_xZ_yP_wO_v$, wherein A is alkali metal, Z is selected from the group consisting of zinc and magnesium, P is phosphorous, O is oxygen, x is about 2 to 3.8, y is about 0.1 to 1.0, the ratio x/y is about 2 to 3.8, v is about 7 to 10, w is about 2 to 3, the ratio v/w is about 3.3 to 3.8, and about 40 to 85 weight percent water.

6. The composition of claim 5 which includes about 0.001 to 0.1 weight percent antifoaming agent selected from the group consisting of nonionic surface active agents, silicone antifoam agents, aliphatic alcohols of 10 carbons or more, organic phosphates and phthalates.

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U.S. Cl. X.R.

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