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ANTI-FREEZE COMPOSITION

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This invention relates to a composition of cooling fluid possessing lubricating properties and to a method for cooling engines with the aforesaid liquid.

This application is a continuation-in-part of application Serial No. 352,280, filed April 30, 1953, now abandoned.

The dissipation of heat from combustion engines is done either by air-cooling or liquid-cooling. In the case of liquid-cooling systems, liquids which do not freeze at ambient temperatures have to be chosen. Hence, for winter operations of automobiles and stationary outdoor engines, mixtures of alcohol and water have been widely used.

In order to improve the thermal efficiency of liquid-cooling systems, forced circulation of the liquid is generally practiced. This introduces the question of lubrication of the sealed-type pump, which is used in the majority of current automobiles. Alcohol-water mixtures do not possess lubricating properties, and, therefore, the circulating pumps are subject to friction problems. Frequently, friction develops between the carbon washer and adjacent metal parts of the pump. This friction usually manifests itself by a noise described as a "squeak" or "squeal" which, because of its high pitch, causes considerable discomfort for the operator and occupants of the vehicle.

Inasmuch as water pumps of the aforesaid character are so well known, and are illustrated in automotive manuals such as those for Ford, Chevrolet, Pontiac, Studebaker, Nash and others, a drawing or sketch of the same is not considered necessary herein and has been omitted.

One of the known expedients for remedying the lack of lubrication in circulating pumps has been the use of emulsifiable mineral oils, commonly termed "soluble oils." This type of oil usually consists of a mixture of mineral oil and an alkali soap of a petroleum sulfonic acid and/or fatty or rosin acid. Soaps, particularly those of fatty and/or rosin acids, are prone to react with calcium and magnesium salts in the cooling water, and the resulting salts are insoluble in water. A similar reaction can take place between soaps and rust or other metal oxides or hydroxides present in the cooling system. In addition, such soaps can be decomposed by the action of acidic components introduced into the cooling system through "blow-by" past the head gasket. As a result, the mineral oil dispersions are unstable and total separation of the mineral oil usually occurs within a short time, as indicated by a clarification of the coolant. Mineral oil freed in this manner will adhere tightly to internal surfaces of the cooling system, thereby interfering with heat transfer. In some cases, the mineral oil or a substantial portion thereof, due to its considerably lower specific gravity as compared with that of the coolant, will tend to rise as an oily scum to the highest point in the cooling system. That is, an oily scum forms in the upper radiator tank and such oil is no longer available

for further lubrication of the pump. In effect, then, the lubricating effect is only of temporary duration. Attempts to remedy this situation by providing an excess of emulsifier are unrewarding since foaming difficulties arise. Furthermore, both the mineral oil and the emulsifiers attack the type of rubber commonly used in cooling systems in the form of hose connections, and cause swelling and eventual disintegration of the rubber connections.

It is an object of this invention, therefore, to provide a liquid cooling fluid having lubricating properties for internal combustion engines. It is also an object of this invention to provide a liquid cooling fluid having the capacity to lubricate the circulating water pump in the liquid-cooling system of a combustion engine. Another object of the invention is to provide a method for lubricating said sealed-type water pump. Still another object is to provide stable dispersions of a lubricant without the use of emulsifiers or dispersants with their attendant shortcomings, other than the alcohol or alcohol blends. It is still a further object to provide a simple composition which can be formulated with a minimum of effort; one which is free from disadvantages of prior compositions. Another object is to provide a composition characterized by excellent heat transfer capacity, anti-foaming properties and not harmful to rubber. Other objects of the invention will be apparent from the following descriptive material.

These objects are realized by the use of certain water-insoluble polyoxyalkylene glycols in conjunction with conventional alcohol coolants, such as methyl, ethyl and propyl alcohols. More specifically, the glycols in question are water-insoluble polyoxypropylene glycols and polyoxybutylene glycols. The aforesaid objects are also realized by the use of aliphatic monoethers of polypropylene glycols in which ether the ether oxygen is attached to a propylene group and is also attached to an aliphatic group having from one to four carbon atoms.

It will be recognized that substantial water-insolubility of the glycols and glycol ethers contemplated herein, is an indirect measure of the molecular weight thereof. In general, the molecular weight of the glycols is above about 1000, and is above about 400 for the glycol ethers.

The polyoxyalkylene glycols used herein are water-insoluble and have molecular weights above about 1000. One group of these polyoxyalkylene glycols can be represented by the following general formula

$$H.(O.C_2H_3.CH_3)_x.OH$$

wherein x is a whole number. These glycols are described by Carbide and Carbon Chemicals Corporation in their Bulletin "Polypropylene Glycols," under date of July 1949, and by Dow Chemical Company in their brochure "Dow Polypropylene Glycols," 1953. They are also described in the text "Glycols" of George O. Curme and Franklin Johnston; Reinhold Publishing Company, New York, 1952. Another description is found in the "Encyclopedia of Chemical Technology," of Kirk and Othmer.

Another group of polyoxyalkylene glycols also useful herein are the polybutylene glycols.

Both of the above group of polyoxyalkylene glycols can be represented by the general formula

$$H.(O.R)_x.OH$$

wherein x is a whole number, and wherein $(O.R)_x$ in one case is a polypropylene oxide and in the second case is a polybutylene oxide.

The polyoxyalkylene glycols of this invention are characterized by the following properties: substantial insolubility in water, and viscosities of at least about 350 seconds, Saybolt, at 100° F. Preferred of such glycols

are those having viscosities above about 500 seconds, Saybolt, at 100° F.

Typical, and advantageous, glycols of the character contemplated herein are those marketed by the Dow Chemical Company, as "Polyglycols." Several of these glycols are shown below in Table I.

Table I

	P 1200	P 2000	P 3000	P 4000
Molecular Weight (Average)	1,200	2,000	3,000	4,000
Specific Gravity, 25/25° C	1.003	1.003	1.001	1.001
Viscosity, Cstks., at 100° F	93.1	164	351	545
Flash Point, °F	460	445	440	440
Pour Point, °F	−40	−38	−15	−15

The aliphatic monoethers of polypropylene glycols contemplated herein are also water-insoluble and have molecular weights above about 400. They are formed by reacting an aliphatic monohydric alcohol and propylene oxide, as shown in Patent No. 2,448,664, issued Sept. 7, 1948, to H. F. Fife and F. H. Roberts, and as shown also in the text "Motor Oils and Engine Lubrication," Carl W. Georgi, Reinhold Publishing Corporation, 1950, pages 226 through 232 and 253. They are also described in the following articles:

J. C. Kratzer et al., "New Synthetic Lubricants," S.A.E. Transactions, 228–237 (1946).

J. M. Russ "Ucon Synthetic Lubricants and Hydraulic Fluids," ASTM Special Publication No. 77, "Symposium on Snythetic Lubricants," Annual ASTM Meeting, Atlantic City, N.J. (June 1947).

The glycol ethers are characterized by viscosities of at least about 60 seconds Saybolt at 100° F. Preferred are those glycol ethers having viscosities above about 300 seconds, Saybolt, at 100° F. Particularly preferred of such glycol ethers is a monobutyl ether of a polypropylene glycol the molecular weight of the ether being about 1400 and its viscosity being about 625 seconds, Saybolt, at 100° F.

Particularly advantageous polyoxyalkylene glycol ethers for the present invention are those of the "Ucon" LB series of glycols marketed by Carbide and Carbon Chemicals Company. Properties of representative members of this series are as follows:

Table II

	Ucon Grade					
	LB-65	LB-285	LB-525	LB-625	LB-1145	LB-1715
Molecular Weight (Plus-Minus 10%)	400	1000	1300	1400	1700	1900
Specific Gravity @ 60° F	.954	.992	1.000	1.000	1.003	1.004
Viscosity, Saybolt Universal at 100° F	65	285	525	625	1145	1715
Flash, COC, °F	275	425	430	430	430	430
Pour Point, °F	−70	−40	−30	−25	−20	−10

As contemplated herein a polyoxyalkylene glycol or glycol ether is selected such that when combined with an anti-freeze alcohol (such as methanol) and the alcohol is admixed with water in the strongest anti-freeze concentration proposed the solubility limit of the glycol or glycol ether is exceeded and the glycol or glycol ether separates as a dispersed phase. Dependent upon the exact nature of the alcohol coolant, glycol and/or glycol ether selected this concentration will be from about 0.05 percent by volume to about 5.0 percent by volume, and preferably from about 0.25 to about 2.0 percent by volume of the alcohol.

The amount of alcohol used in any case, obviously, is dependent upon the degree of freezing protection desired. Generally, from about ten percent by volume to about fifty percent by volume of alcohol is used with from about ninety percent to about fifty percent by volume of water. Expressed in another manner, from about 0.025 to about 2.5 of glycol or glycol ether of the aforesaid character, is used with from about fifty to about ninety percent by volume of water, and with the balance to one hundred percent by volume being alcohol. Preferred compositions, however, are those containing from about 0.05 to about 0.5 percent by volume of glycol or glycol ether, and containing quantities of water and alcohol such as indicated above.

In connection with the quantity or concentration of glycol or glycol ether, it has been found that when the values above are exceeded, there is a sacrifice in freezing point protection without any further gain in lubricating value. Correspondingly, when the quantity or concentration of glycol or glycol ether is substantially less than the values recited above, the compositions containing the same lubricate effectively for only relatively short periods of use, since the glycol or glycol ether tends to become depleted. Similarly, when substantially less than fifty percent by volume of water is used with the alcohol and glycol and/or glycol ether, the boiling point of the resulting composition is lowered excessively and alcohol is lost therefrom by volatilization. Furthermore, when excessive water is used, freezing protection is negligible.

Thus, a glycol or glycol ether, in the concentrations recited above, can be added to an anti-freeze grade of alcohol as sold to the trade. Then, too, a composition comprising the glycol and/or glycol ether and the alcohol in said concentrations, can be prepared and sold as such. The lubricant can be added to a mixture of anti-freeze alcohol and water; however, this procedure is less advantageous than the procedures mentioned immediately above.

The glycols and/or glycol ethers and anti-freeze alcohols form clear solutions when the foregoing concentrations are used. When these solutions are diluted with water, the solubility of the glycol and/or glycol ether is exceeded and it drops out of solution and spontaneously forms a dispersion. As the latter flows through the pump, the glycol and/or glycol ether lubricates the pump and assures noiseless operation.

Practical tests on noisy water pumps in automobile cooling systems operating on conventional prior art anti-freeze compositions, have been made. The elimination of squeaks in the pumps was noticed immediately upon the use of compositions of this invention. For instance, a 1942 Chevrolet, a 1948 Studebaker, a 1938 Chevrolet, a 1950 Studebaker and a 1948 Nash were selected for test because all water pumps exhibited annoying squeal when the respective cooling systems were operating on a fill of straight water. This noise was particularly noticeable at low engine speeds such as prevailing during idling. The cooling systems of the first two vehicles were filled with a mixture containing 25% by volume of a conventional methanol anti-freeze, the balance being water. The other vehicles were serviced with materials of the present invention, consisting of 25% by volume of a conventional methanol anti-freeze modified by the addition of 0.5% by volume of the monobutyl ether of polypropylene glycol, having a molecular weight of about 1400 and about 1900 in the case of the last vehicle. These solutions, therefore, comprised 0.125% by volume of polypropylene glycol monobutyl ether, 24.375% by volume of conventional methanol anti-freeze and the balance water.

When the vehicles containing prior art anti-freeze were operated subsequently, squeaking noises continued intermittently during the entire winter. In contrast, vehicles operating on compositions of the present invention were distinguished by noiseless pump operation immediately following installation and continued to operate without squeal for the full length of the season.

As contemplated herein, the polyoxyalkylene glycols and/or glycol ethers used in conjunction with the above-recited conventional coolants, are advantageous in providing an effective method for lubricating moving parts in a circulating cooling system. A liquid cooling medium containing one or more of said polyoxyalkylene glycols and/or glycol ethers is brought in contact with the moving parts, whereupon the polyoxyalkylene glycol or polyoxyalkylene glycol ether becomes associated with the surfaces of said moving parts and thereby lubricate the same.

It is to be understood that conventional corrosion inhibitors, dyes, and other additives used in alcohol anti-freeze compositions can be used in the compositions of this invention. The polyoxyalkylene glycols and glycol ethers do not adversely affect such materials, nor are they adversely affected by such materials. Representative of such corrosion inhibitors are borax, sodium nitrite and disodium phosphate; representative of such dyes, which are used primarily for brand identification, are methyl violet (empirical formula, $C_{24}H_{28}N_3Cl$) and Patent Blue (empirical formula, $C_{37}H_{35}N_2O_6S_2Na$). One typical formulation, for example, calls for methyl violet 2B in an amount of 0.01 pound per 100 gallons of methanol.

It is also to be understood that the invention is not to be limited to anti-freeze compositions for automotive cooling systems or to a method for lubricating such systems, but is broadly applicable to anti-freeze compositions for any internal combustion engine cooling systems and to a method for lubricating the latter. Typical of other such systems are: aircraft cooling systems, marine cooling systems, and stationary diesels.

I claim:

1. An anti-freeze composition for addition to the water in the cooling system of an internal combustion engine, consisting essentially of: from about 0.05 to about 5.0 percent by volume of a lubricant consisting of a water-insoluble polyoxyalkylene glycol, from about 99.95 to about 95.0 percent by volume of a saturated monohydric alcohol having from one to three carbon atoms per molecule, said polyoxyalkylene glycol being the sole glycol material present in the composition and being selected from the group consisting of a polyoxyalkylene glycol having a molecular weight above about 1000 and being represented by the following general formula

$$H.(O.C_2H_3.CH_3)_x.OH$$

wherein x is a whole number, a polyoxyalkylene glycol having a molecular weight above about 1000 and being represented by the following general formula

$$H.(O.R)_x.OH$$

wherein x is a whole number, and wherein $(O.R)_x$ is a polyoxybutylene group, and an aliphatic monoether of a polypropylene glycol, which ether has a molecular weight above about 400 and in which ether the ether oxygen which is attached to a propylene group, is also attached to an aliphatic group having from one to twenty carbon atoms.

2. An anti-freeze composition for addition to the water in the cooling system of an internal combustion engine, consisting essentially of: from about 0.05 to about 5.0 percent by volume of a lubricant consisting of a water-insoluble polyoxyalkylene glycol, said water-insoluble glycol being the sole glycol present in the composition, and from about 99.95 to about 95.0 percent by volume of a saturated monohydric alcohol having from one to three carbon atoms per molecule, said glycol having a molecular weight above about 1000 and being represented by the general formula

$$H.(O.C_2H_3.CH_3)_x.OH$$

wherein x is a whole number.

3. An anti-freeze composition for addition to the water in the cooling system of an internal combustion engine, consisting essentially of: from about 99.95 to about 95.0 percent by volume of an alcohol having from one to three carbon atoms per molecule and from about 0.05 to about 5.0 percent by volume of a lubricant consisting of a water-insoluble, aliphatic monoether of a polypropylene glycol, which ether is the sole ether present in the composition and has a molecular weight above about 400 and in which ether the ether oxygen is attached to a propylene group and is also attached to an aliphatic group having from one to four carbon atoms.

4. The anti-freeze composition of claim 1 in which the glycol material is present in an amount from about 0.25 to about 2.0 percent by volume.

5. The anti-freeze composition of claim 3 in which the glycol material is a monobutyl ether of a polypropylene glycol, the molecular weight of said ether being about 1400.

6. An anti-freeze composition for the cooling system of an internal combustion engine, consisting essentially of: from about 0.025 to about 2.5 percent by volume of a lubricant consisting of a water-insoluble polyoxyalkylene glycol, from about fifty to about ninety percent by volume of water and the balance a saturated monohydric alcohol having from one to three carbon atoms per molecule, said polyoxyalkylene glycol being the sole glycol material present in the composition and selected from the group consisting of a polyoxyalkylene glycol having a molecular weight above about 1000 and being represented by the following general formula

$$H.(O.C_2H_3.CH_3)_x.OH$$

wherein x is a whole number, a polyoxyalkylene glycol having a molecular weight above about 1000 and being represented by the following general formula

$$H.(O.R)_x.OH$$

wherein x is a whole number, and wherein $(O.R)_x$ is a polyoxybutylene group, and an aliphatic monoether of a polypropylene glycol, which ether has a molecular weight above about 400 and in which ether the ether oxygen which is attached to a propylene group, is also attached to an aliphatic group having from one to twenty carbon atoms.

7. An anti-freeze composition for the cooling system of an internal combustion engine, consisting essentially of: from about 0.025 to about 2.5 percent by volume of a lubricant consisting of a water-insoluble polyoxyalkylene glycol, from about fifty to about ninety percent by volume of water and the balance a saturated monohydric alcohol having from one to three carbon atoms per molecule, said polyoxyalkylene glycol being the sole glycol material present in the composition and having a molecular weight above about 1000 and being represented by the general formula $H.(O.C_2H_3.CH_3)_x.OH$ wherein x is a small whole number.

8. An anti-freeze composition for the cooling system of an internal combustion engine, consisting essentially of: from about 0.025 to about 2.5 percent by volume of a lubricant consisting of a water-insoluble, aliphatic monoether of a polypropylene glycol, from about fifty to about ninety percent by volume of water and the balance a saturated monohydric alcohol having from one to three carbon atoms per molecule, said glycol ether being the sole glycol ether present in the composition and having a molecular weight above about 400 and in which ether the ether oxygen is attached to a propylene group and is also attached to an aliphatic group having from one to four carbon atoms.

9. The anti-freeze composition of claim 6 in which the polyoxyalkylene glycol is present in an amount from about 0.05 to about 0.5 percent by volume.

10. The anti-freeze composition of claim 8 in which the polyoxyalkylene glycol is a monobutyl ether of a polyproylene glycol, the molecular weight of said ether being about 1400.

11. An anti-freeze composition for the cooling system of an internal combustion engine, consisting essentially of: from about 0.025 to about 2.5 percent by volume of a lubricant consisting of a water-insoluble polyoxyalkylene glycol, from about fifty to about ninety percent by volume of water and the balance a saturated monohydric alcohol having from one to three carbon atoms per molecule, said polyoxyalkylene glycol being the sole glycol material present in the composition and having a molecular weight above about 1000 and being represented by the general formula $H.(O.R)_x.OH$ wherein x is a small whole number, and $(O.R)_x$ is a polybutylene oxide.

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