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OIL PHASE ANTIFREEZE INHIBITOR

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This invention relates to a novel inhibitor composition and an antifreeze mixture which are effective in minimizing the corrosion accompanying the use of permanent type antifreeze mixtures in the cooling systems of internal combustion engines and similar devices. This application is a continuation in part of my application Serial No. 327,703, filed December 23, 1952, now abandoned.

Antifreeze mixtures are essentially of two types. In the non-permanent type, a water-miscible, low-boiling monohydroxy alcohol is used as a freezing point depressant for water; methyl alcohol, ethyl alcohol, propyl alcohol and mixtures thereof are normally used in the non-permanent type antifreezes. The permanent type antifreezes are water-miscible, high-boiling polyhydroxy alcohols; at the present time, ethylene glycol is the base most commonly used in permanent type antifreezes, but glycerine and other glycols such as propylene glycol, diethylene glycol, and mixtures thereof are also used. The novel inhibitor composition of this invention is for use with permanent type antifreezes.

It is well known that both permanent and non-permanent type antifreezes cause serious corrosion of metals during service wherein they are normally in admixture with water. The aqueous antifreeze mixtures cause serious corrosion of steel, brass, copper, aluminum and solder which are present in the circulating cooling systems of internal combustion engines. A large number of corrosion inhibitors have been employed to inhibit the corrosive action of the aqueous antifreeze mixtures in service and many special formulations have been devised for decreasing the corrosive tendencies of permanent and non-permanent antifreezes. One successful means for alleviating the corrosive tendency of permanent antifreezes involves adding a high-boiling hydrocarbon fraction such as a lubricating oil to the antifreeze in an amount equivalent to about 0.5 to 2 percent of the glycol component of the antifreeze. This invention discloses a multi-component additive which substantially improves the corrosion-inhibiting action of a hydrocarbon oil phase in permanent antifreeze mixtures.

The present invention involves the discovery that a superior oil phase inhibitor for permanent type antifreezes is formed by adding to a high-boiling hydrocarbon fraction a mixture comprising a salt of a petroleum sulfonate, a polyvalent metal salt of an alkyl thiophosphate, a divalent salt of a naphthenic acid and a fatty acid partial ester of an aliphatic polyol containing at least three hydroxyl groups. Advantageously, the mixture added to the high-boiling hydrocarbon fraction contains another component which imparts improved anti-corrosive action to the resulting antifreeze mixture; this additional component is a sulfurized terpene. The superior oil phase inhibitor of this invention, which normally constitutes 0.05 to 2 volume percent of the total non-aqueous antifreeze mixture, comprises 30 to 60 weight percent mineral oil, 20 to 40 percent metal salt of

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petroleum sulfonate, 5 to 20 percent polyvalent metal salt of an alkyl thiophosphate, 5 to 12 percent divalent metal naphthenate salt and 5 to 15 percent of a fatty acid partial ester of an aliphatic polyol. In the preferred inhibitor, sulfurized terpene normally constitutes 0.5 to 3 weight percent of the total oil phase inhibitor.

A particularly preferred oil phase inhibitor contains the barium salts of the petroleum sulfonate and of the alkyl thiophosphate, and the zinc salt of a naphthenic acid; in this preferred inhibitor, the fatty acid partial ester of a polyol advantageously comprises a mixture of oleic acid partial esters of glycerine and sorbitan.

The novel oil phase inhibitor of this invention is normally used to supplement the action of inorganic corrosion inhibitors which are soluble to some extent in glycols. Inorganic salts such as borate salts, trisodium phosphate salts and sodium silicate salts impart reserve alkalinity and minimize corrosion in permanent antifreezes. In general, alkaline earth metal borates, alkali metal phosphates and silicates are widely used as glycol-soluble corrosion inhibitors. The superiority of the oil phase of this invention will be demonstrated in connection with antifreezes containing soluble inorganic salt inhibitors. A calcium borate-inhibited ethylene glycol antifreeze containing 1 percent oil phase comprising lube oil, basic barium petroleum sulfonate, barium alkyl thiophosphate, a mixture of oleic acid partial esters of glycerine and sorbitan, zinc naphthenate and sulfurized terpene displays exceptional freedom from corrosion during service.

The hydrocarbon fraction employed in the oil phase inhibitor is usually a lube oil or a high boiling gas oil fraction. Both paraffin-base and naphthene-base high-boiling hydrocarbon fractions can be used, but naphthene base oils are preferred for formulating the oil phase inhibitor of this invention. The naphthene-base oils are normally used because of their low pour points. A particularly preferred naphthene base oil is a lube oil fraction having a Saybolt Universal viscosity at 100° F. of about 70 and a pour point of -25° F.

The specific gravity of the oil phase of this invention is less than that of the glycol permanent antifreezes so that it forms a supernatant layer when combined therewith. This characteristic of the oil phase is beneficial in insuring complete transfer of the oil phase during mixing of the antifreeze with water.

The petroleum sulfonate salts used in the novel oil phase inhibitor of this invention are obtained by reaction of concentrated sulfuric acid (90 percent minimum) with high-boiling hydrocarbon fractions in the lube oil range followed by neutralization of the resulting petroleum sulfonate fraction with alkali. The preparation of petroleum sulfonate salts is too well known to need further explanation and description herein. The alkaline earth metal petroleum sulfonates, particularly basic barium sulfonate, are sulfonates for use in the invention. Basic barium sulfonate is the term used to designate products resulting from reaction of petroleum sulfonic acids with barium hydroxide in such proportions that the resulting mixture contains one free hydroxyl group. The basic alkaline earth metal petroleum sulfonates which are generally either barium or calcium salts are superior to the alkali metal petroleum sulfonates and the fully neutralized alkaline earth metal petroleum sulfonates in imparting anti-corrosive properties to the novel oil phase inhibitor of this invention. The basic alkaline earth metal petroleum sulfonates and other alkali metal and alkaline earth metal sulfonates usually comprise 20 to 40 weight percent of the total oil phase inhibitor with a concentration range of 25 to 30 percent being preferred for this component.

The polyvalent salts of alkyl thiophosphates are produced by the reaction of divalent or trivalent metals with

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alkyl thiophosphates which may be produced by reaction of phosphorus pentasulfide with monohydroxy alcohols. Alcohols having six to twelve carbon atoms may be employed to form the alkyl thiophosphate. Representative alcohols include lauryl, cyclohexyl, capryl, octyl and methylcyclohexyl alcohol. The metal salts are readily formed by heating the alkyl thiophosphate with an excess of powdered metal or metal oxide at a temperature about 200° to 350° F. The alkyl thiophosphate salts, such as barium methylcyclohexyl thiophosphate, calcium lauryl thiophosphate, zinc capryl thiophosphate and barium capryl thiophosphate are readily soluble in mineral oil. The polyvalent salt of an alkyl thiophosphate usually constitutes 5 to 20 percent of the total oil phase inhibitor and more usually 8 to 18 percent of the total oil phase inhibitor with a concentration range of 10 to 15 percent being preferred.

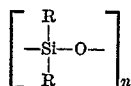
The fatty acid partial ester of an aliphatic polyol containing at least three hydroxyl groups is formed by partial esterification of a polyhydroxy alcohol such as glycerine, sorbitol, sorbitan, mannitol, penta-erythritol, etc. with a fatty acid such as stearic acid, oleic acid, linoleic acid, etc. Oleic acid is the preferred fatty acid and the polyhydroxy alcohol preferably comprises a mixture of glycerine and a six carbon hexahydroxy alcohol such as sorbitol, mannitol or their inner anhydrides. A mixture of sorbitan sesqui-oleate and glyceryl mono-oleate in an approximate ratio of five parts by weight of the former to one part by weight of the latter have proven to be a very effective mixture.

The fatty acid-polyhydroxy alcohol partial ester normally constitutes 5 to 15 percent of the total oil phase inhibitor with the preferred concentration falling in the range of 9 to 12 percent. The incorporation of 10 to 11 weight percent of a 4:1 mixture of sorbitan sesqui-oleate and glyceryl mono-oleate in the oil phase inhibitor has resulted in the production of a particularly active oil phase inhibitor.

The divalent naphthenate salt component of the oil phase inhibitor is a well known chemical which is formed by neutralization of naphthenic acids separated from petroleum. Barium, calcium, divalent copper and zinc salts are generally used in formulating the oil phase inhibitor; the zinc salt has proven particularly active. The divalent naphthenate salt constitutes 5 to 10 percent of the total oil phase inhibitor.

The sulfurized terpene component of the oil phase inhibitor is obtained by reaction of hydrogen sulfide or sulfur with terpenes such as pinene, limonene, terpinene, dipentene and mixtures thereof. The procedures employed for preparation of sulfurized terpenes are also well known in the art, and need no further description herein. The sulfurized terpene component normally comprises a minor portion of the oil phase inhibitor in the range of 0.5 to 2.5 weight percent.

It is also recommended that a small amount of silicone be included in the oil phase inhibitor when it is used in conjunction with antifreeze mixtures that have a tendency to foam. Silicones having a general formula



wherein R is an aliphatic or an aryl radical are known antifoam agents. Their use in a concentration of about 1 to 50 parts per million of the oil phase inhibitor makes the inhibitor an effective antifoam agent.

In order to display superior anticorrosive properties in permanent type antifreezes, the oil phase inhibitor must contain metal petroleum sulfonate, polyvalent metal alkyl thiophosphate, divalent metal naphthenate salt and fatty acid polyhydroxy alcohol partial esters in the concentrations indicated heretofore, namely 30 to 60 percent mineral oil (e.g., about 40%), 20 to 40 percent metal

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petroleum sulfonate (e.g., about 29% basic barium petroleum sulfonate) 5 to 20 percent polyvalent metal alkyl thiophosphate (e.g., about 13% barium alkyl thiophosphate, in which said alkyl group has from 6 to 12 carbon atoms, such as a methylcyclohexyl group), 5 to 12 percent naphthenate salt (e.g., about 7% zinc naphthenate), and 5 to 20 percent partial ester (e.g., about 10% of a mixture comprising oleate partial esters of glycerine and sorbitan, such as about 2% glyceryl monooleate and about 8% sorbitan sesquioleate). However, the addition of minor quantities of sulfurized terpene in an amount less than 10 percent (e.g., about 1%) of the total inhibitor composition results in the production of a superior oil phase inhibitor. An oil phase inhibitor which has proven particularly effective comprises 39.6 percent mineral oil, 29.3 percent basic barium petroleum sulfonate, 13.2 percent barium methylcyclohexyl thiophosphate, 8.4 percent sorbitan sesqui-oleate, 1.8 percent glyceryl mono-oleate, 6.6 percent zinc naphthenate and 1.1 percent sulfurized terpene. When 1 percent of this oil phase inhibitor is used in connection with ethylene glycol having dissolved therein about 1% by weight calcium borate inhibitor, the resulting anti-freeze has proven to be exceptionally corrosion-free in service. The composition of this superior complete antifreeze is as follows:

Glycol phase:	Weight percent
Ethylene glycol	97.92
Ca(OH) ₂	0.55
H ₃ BO ₃	1.53
Oil phase—1 volume percent of glycol phase:	
Naphthene base lube oil	39.6
Basic barium sulfonate	29.3
Barium methylcyclohexyl thiophosphate	13.2
Sorbitan sesqui-oleate	8.4
Glyceryl mono-oleate	1.8
Zinc naphthenate	6.6
Sulfurized terpene	1.1

In the above table, superior anticorrosive properties of the multi-component oil phase inhibitor of this invention are clearly demonstrated. The improvement imparted to anti-freeze mixtures by using the novel oil phase inhibitors of this invention will be demonstrated with calcium borate-inhibited glycol mixtures. Actual service conditions are simulated by using water antifreeze mixtures formed by adding 40 parts by volume of anti-freeze mixture to 60 parts by volume of water.

The compositions of the glycol antifreezes tested are as follows:

A. 97.92 percent ethylene glycol, 0.55 percent Ca(OH)₂ and 1.53 percent H₃BO₃.

B. A plus 1 volume percent naphthene base lube oil having a Saybolt Universal viscosity at 100° F. of about 200.

C. A plus 2 volume percent oil phase comprising 60 weight percent naphthene lube oil having a Saybolt Universal viscosity at 100° F. of about 70 and 40 weight percent basic barium sulfonate.

D. A plus 1 volume percent oil phase comprising 39.2 weight percent naphthene lube oil having a Saybolt Universal viscosity at 100° F. of about 70, 6.6 weight percent zinc naphthenate, 8.4 weight percent sorbitan sesquioleate, 1.8 percent glyceryl mono-oleate, 39.2 weight percent barium salt of alkyl thiophosphate and 4.8 weight percent sulfurized terpene.

E. A plus 1 volume percent oil phase comprising 56.4 weight percent naphthene lube oil having a Saybolt Universal viscosity at 100° F. of about 70, 29.3 percent basic barium sulfonate, 13.2 percent barium salt of alkyl thiophosphate and 1.1 percent sulfurized terpene.

F. A plus 1 volume percent oil phase comprising 39.6 weight percent naphthene lube oil having a Saybolt Universal viscosity at 100° F. of about 70, 29.3 weight percent basic barium sulfonate, 13.2 weight percent barium

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salt of alkyl thiophosphate, 8.4 weight percent sorbitan sesqui-oleate, 1.8 weight percent glyceryl mono-oleate, 6.6 weight percent zinc naphthenate and 1.1 weight percent sulfurized terpene.

The above compositions were compared in the so-called simulated engine test. In this test, the test unit consists of a circulating cooling system having an automotive water pump forcing the 40 percent aqueous solution of the antifreeze in series through a test reservoir, then in parallel through two radiators from automobile heaters, and the combined streams from the radiators are then forced past an electric heater and returned to the suction side of the pump. The anti-freeze solution is maintained at 190° 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 aluminum, brass, copper and steel specimens having dimensions of ½" x 4" x ¼" and a 4" length of ⅛" wire solder are suspended in the circulating antifreeze 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 simulates the actual service conditions of the antifreeze in use in the circulating cooling system of an internal combustion engine.

A comparison of aqueous solutions of antifreezes A through F in the simulated engine test proves the effectiveness of the novel oil phase inhibitors of this invention. The comparison was made with aqueous compositions comprising 60 percent water and 40 percent antifreeze. The results are shown in the following table showing the weight loss in milligrams of the metal strips after 300 and 600 hours in the simulated engine test:

300 HOUR TEST

	A	B	C	D	E	F
Aluminum.....	189	143	567	255	151	120
Brass.....	16	19	27	17	20	13
Solder.....	94	47	30	37	39	20
Copper.....	18	10	23	25	20	14
Steel.....	539	250	308	441	202	108

600 HOUR TEST

	A	B	C	D	E	F
Aluminum.....	248	-----	707	100	124	124
Brass.....	22	-----	23	15	37	17
Solder.....	160	-----	133	81	142	77
Copper.....	15	-----	12	31	12	19
Steel.....	845	-----	896	1,094	298	361

The data in the table clearly illustrates the superior inhibiting properties of the improved oil phase inhibitor of this invention. The improved results are clearly attributable to the synergistic action of the components of the multi-component oil phase since oil phases containing most of the components do not approach the inhibiting properties possessed by the improved oil phase inhibitor of the invention represented by Composition F.

Composition A containing no oil phase inhibitor showed high weight losses on solder and steel in both the 300 and 600 hour test. The addition of an oil phase consisting of a naphthene base lube oil substantially reduced the solder and steel corrosion as shown by Composition B. The addition of basic barium sulfonate to the oil phase (Composition C) effected an improvement in the solder corrosion over Composition B, but showed inferior aluminum, copper and steel corrosion. Composition D, in which the oil phase contains zinc naphthenate, sorbitan

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sesqui-oleate, glyceryl mono-oleate, barium alkyl thiophosphate and sulfurized terpene, all of the components of the superior inhibitor of this invention with the exception of basic barium sulfonate, showed improvement in solder corrosion and aluminum corrosion, but the steel corrosion was still very high. Composition E, in which the oil phase contains basic barium sulfonate, a barium salt of an alkyl thiophosphate and sulfurized terpene, showed improved steel protection, but relatively poor solder protection; Composition E contains all the components of the improved inhibitor of this invention with the exception of zinc naphthenate and the polyol partial esters. Composition F, the improved inhibitor of the invention, displayed excellent protection for all the strips tested with the solder and steel protection being particularly noteworthy. The superior results obtained with Composition F can only be attributed to the synergistic action of the combination of components present therein. The steel protection obtained by the addition of basic barium sulfonate to the other ingredients of the mixture would certainly not be expected from a comparison of the results obtained with Composition C, containing basic barium sulfonate and Composition D, containing all of the ingredients of the novel inhibitor with the exception of basic barium sulfonate.

While the superiority of the oil phase inhibitors of this invention has been demonstrated employing inhibited glycols as a standard, it is understood that a similar improvement is effected by using the oil phase of this invention in conjunction with straight glycol as an antifreeze. Since the reserve alkalinity provided by inorganic salts such as calcium borate, sodium phosphate, etc., substantially reduces the corrosiveness of glycol mixtures, particularly after prolonged periods of service, the novel oil phase inhibitors of this invention are ordinarily used in conjunction with inhibited glycol.

Obviously, many modifications and variations of the invention, as hereinbefore 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 antifreeze mixture comprising a polyhydroxy alcohol freezing point depressant and 0.5 to 2% by volume of an insoluble oil phase inhibitor comprising, by weight, 30 to 60% mineral oil, 20 to 40% of a metal salt of petroleum sulfonate, 8 to 18% of a polyvalent salt of an alkyl thiophosphate wherein said alkyl group has 6 to 12 carbon atoms, 5 to 12% of a divalent metal naphthenate and 5 to 15% of a fatty acid partial ester of an aliphatic polyol having at least 3 hydroxyl groups.

2. An antifreeze mixture comprising a polyhydric alcohol freezing point depressant and 0.5 to 2% by volume of an insoluble oil phase inhibitor comprising, by weight, 30 to 60% mineral oil, 20 to 40% basic barium petroleum sulfonate, 8 to 18% basic barium alkyl thiophosphate in which said alkyl group has from 6 to 12 carbon atoms, 5 to 12% zinc naphthenate and 5 to 15% of a mixture comprising oleate partial esters of glycerin and sorbitan.

3. An antifreeze mixture comprising a polyhydroxy alcohol freezing point depressant and 0.5 to 2% by volume of an insoluble oil phase inhibitor comprising, by weight, approximately 40% mineral oil, 29% basic barium petroleum sulfonate, 8% sorbitan sesqui-oleate, 2% glyceryl mono-oleate, 13% basic barium methylcyclohexyl thiophosphate, 7% zinc naphthenate and 1% sulfurized terpene.

4. An antifreeze mixture according to claim 1 in which said freezing point depressant is ethylene glycol.

5. An antifreeze mixture in accordance with claim 1 wherein said oil phase inhibitor also comprises less than 10% sulfurized terpene.

6. An antifreeze mixture in accordance with claim 1 wherein said oil phase inhibitor also comprises 0.5 to 2.5% sulfurized terpene.

7. An antifreeze mixture comprising a polyhydroxy alcohol freezing point depressant and 0.5 to 2% by volume of an insoluble oil phase inhibitor comprising, by weight, 30 to 60% mineral oil, 20 to 40% basic barium petroleum sulfonate, 10% of a mixture comprising oleate partial esters of glycerine and sorbitan, 13% barium alkyl thiophosphate, in which said alkyl group has from 6 to 12 carbon atoms, and 7% zinc naphthenate.

8. A two-phase antifreeze mixture comprising a polyhydroxy alcohol freezing point depressant and about 1% by weight of calcium borate dissolved therein and 0.5 to 2% by volume of an insoluble oil phase inhibitor comprising, by weight, 30 to 60% mineral oil, 20 to 40% of a metal salt of petroleum sulfonate, 8 to 18% of a polyvalent salt of an alkyl thiophosphate in which said alkyl group has 6 to 12 carbon atoms, 5 to 12% of a divalent metal naphthenate and 5-15% of a fatty acid partial ester of an aliphatic polyol having at least 3 hydroxyl groups.

9. A two phase antifreeze mixture comprising a polyhydroxy freezing point depressant and about 1% by weight of calcium borate dissolved therein, and 0.5-2% by volume of an insoluble oil phase inhibitor comprising, by weight, 30-60% mineral oil, 20-40% basic barium petroleum sulfonate, 8-18% basic barium alkyl thiophosphate in which said alkyl group has from 6-12 carbon atoms, 5-12% zinc naphthenate and 5-15% of a mixture comprising oleate partial esters of glycerin and sorbitan.

10. A two-phase antifreeze mixture comprising ethylene glycol and about 1% by weight of calcium borate dissolved therein, and 0.5-2% by volume of an insoluble oil phase inhibitor comprising approximately 40% mineral

oil, 29% basic barium petroleum sulfonate, 8% sorbitan sesqui-oleate, 2% glyceryl mono-oleate, 13% basic barium methylcyclohexyl thiophosphate, 7% zinc naphthenate and 1% sulfurized terpene.

11. In a method for cooling an internal combustion engine by circulating a coolant comprising water and a polyhydric alcohol freezing point depressant in heat exchange relationship with said engine; inhibiting the corrosion of metal parts of said engine by circulating said coolant therethrough as a mixture containing water, a water miscible polyhydric alcohol freezing point depressant, and 0.5-2% by volume of an oil phase corrosion inhibitor based on said polyhydric alcohol, said oil phase inhibitor comprising, by weight, 30-60% mineral oil, 20-40% basic barium petroleum sulfonate, 8-18% basic barium salt of an alkyl thiophosphate wherein the alkyl group has from six to twelve carbon atoms, 5-12% zinc naphthenate, and 5-15% of a mixture comprising oleate partial esters of glycerine and sorbitan.

12. In a method in accordance with claim 11, said oil phase inhibitor also comprising 0.5-2.5% sulfurized terpene.

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