United States Patent Office

2,765,278

Patented Oct. 2, 1956

2,765,278

OIL PHASE ANTIFREEZE INHIBITOR

Cameron B. Holter and Charles T. Anné, Port Arthur, Tex., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application August 20, 1952, Serial No. 305,506

14 Claims. (Cl. 252—75)

This invention relates to a novel inhibitor composition which is effective in minimizing the corrosion accompanying the use of permanent type antifreeze mixtures in the cooling systems of internal combustion engines and similar devices.

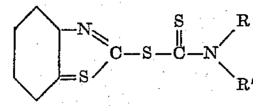
Antifreeze mixtures are essentially of two types. In the non-permanent type, a water-miscible, low-boiling monohydroxy alcohol is used as a freezing point depressant for water; methyl alcohol, ethyl alcohol, propyl alcohol and mixtures thereof are normally used in the non-permanent type antifreezes. 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 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 mixture causes 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 class of compounds 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 addition of a minor portion of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide to a high boiling hydrocarbon fraction. This superior oil phase inhibitor, which normally constitutes 0.05 to 2 volume percent of the total non-aqueous antifreeze mixture, comprises 0.5 to 5 weight percent 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide and 95 to 99.5 weight percent oil phase. It has been discovered that the diethyl compound, namely, 2-benzothiazyl-N,N - diethylthiocarbamyl sulfide is a preferred agent for improving the anti-corrosive action of an oil phase in permanent antifreezes.

A particularly preferred modification of the invention involves use of sperm oil as a component of the oil phase. The addition of sperm oil to the oil phase containing 2-benzothiazyl-N,N-dialkylthiacarbamyl sulfide remarkably improves its anticorrosive properties. A preferred oil phase inhibitor comprises 20 to 79.5 weight percent high boiling hydrocarbon fraction, 20 to 60 percent sperm oil and 0.5 to 5 percent 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide.

The compounds which improve the anticorrosive properties of hydrocarbon oil phase in permanent antifreezes have the following general formula:



wherein R and R′ designate similar or dissimilar alkyl or alkenyl groups such as methyl, ethyl, propyl, propenyl, butyl, butenyl, amyl and pentenyl groups. By far the preferred material is the diethyl compound which is sold commercially as a rubber accelerator under the trade name "Ethylac." While 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide is the preferred agent for use in the novel oil phase inhibitors of this invention, other alkyl and alkenyl derivatives may also be employed, since they are soluble in a hydrocarbon fraction in the concentrations prescribed herein.

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 and sodium silicate impart reserve alkalinity and minimize corrosion in permanent antifreezes. In general, alkalines 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 a hydrocarbon fraction, sperm oil and 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide 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 an SUV at 100° F. of about 200 and a pour point of −35° 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.

Sperm oil is derived from sperm whales and consists mainly of esters of C_{10} to C_{22} acids and C_{14} to C_{20} monohydroxy aliphatic alcohols. A preferred sperm oil is designated 38° bleached winter grade which indicates that it will not congeal at 38° F.

An oil phase inhibitor which has proven particularly effective comprises 0.5 percent 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide, 45 percent sperm oil and 54.5 percent naphthene-base lube oil fraction having an SUV at 100° F. of 200. When 1 percent of this oil phase inhibitor is used in connection with a calcium borate-inhibited ethylene glycol mixture, there is produced an antifreeze which in service has proven particularly free of corrosion on the metal parts of the cooling system of an internal combustion engine. The composition of this superior complete antifreeze is as follows:

Glycol phase:	Weight percent
Ethylene glycol	97.92
$Ca(OH)_2$	0.55
H_3BO_3	1.53

Oil phase—1 volume percent of glycol phase:

	Weight percent
Ethylac	0.5
Sperm oil	45.0
Naphthene lube oil	54.5

In the following tables, the superior anticorrosive properties of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide-containing oil phase inhibitors of this invention are clearly demonstrated. The improvement imparted to antifreeze 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 antifreeze 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 H_3Bo_3.

B. A plus 1 volume percent napthene base lube oil having an SUV at 100° F. of about 200.

C. A plus 1 volume percent oil phase comprising 99.5 weight percent naphthene base lube oil having an SUV at 100° F. of about 200 and 0.5 weight percent Ethylac.

D. A plus 1 volume percent oil phase comprising 0.5 weight percent Ethylac, 45 percent sperm oil, 54.5 percent naphthene base lube oil having an SUV at 100° F. of about 200.

Compositions A, B, C and D 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 then are forced past an electric heater and returned to the suction side of the pump. The antifreeze 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 antifreeze to corrosive acids. Polished and weighed aluminum, brass, copper and steel specimens having dimensions of ½" x 4" x 1/16" 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 thus 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, B, C and D in the simulated engine test proved the effectiveness of oil phase inhibitors containing 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide. The comparison was made with aqueous compositions comprising 60 percent water and 40 percent antifreeze. The corrosion obtained with the standard calcium borate-inhibited antifreeze, that is antifreeze A, is shown in Table I showing the weight loss in milligrams of the metal strips after 300 and 600 hours immersion in the simulated engine test:

TABLE I

	300 Hours, mg.	600 Hours, mg.
Aluminum	264	289
Brass	29	27
Solder	84	151
Copper	21	17
Iron	378	797

Antifreeze B, in which a naphthene base oil was used as an inhibitor, substantially reduced the corrosive effect of the calcium borate-inhibited glycol antifreeze, as shown in Table II in which the experimental data are reported as in the previous table:

TABLE II

		300 hours
Aluminum	mg	143
Brass	mg	19
Solder	mg	47
Copper	mg	10
Iron	mg	250

Antifreeze C, in which an Ethylac-containing oil phase was used, further reduced the aluminum and iron corrosion of the calcium borate-inhibited antifreeze; the aluminum strip showed only 98 mg. and 143 mg. losses after 300 and 600 hours operation respectively; the iron strip showed only 221mg. and 525 mg. losses after 300 and 600 hours operation respectively. Antifreeze C did not show any substantial improvement in brass, solder and copper losses over antifreeze B.

Antifreeze D, which contained the preferred oil phase inhibitor of this invention comprising Ethylac and sperm oil substantially improved the iron corrosive tendencies of the antifreeze over that illustrated by antifreeze C as demonstrated by the fact that the iron strip only showed 99 mg. and 402 mg. losses after 300 and 600 hours respectively; antifreeze D also showed a substantial improvement in solder corrosion, as illustrated by the fact that the solder strip only showed 31 mg. and 67 mg. losses after 300 and 600 hours respectively. Antifreeze D had approximately the same corrosiveness to aluminum as antifreeze C, and was equivalent to antifreeze B and C in its corrosiveness towards brass and copper.

The foregoing data demonstrates that the addition of a 4-component inhibitor containing 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide substantially reduced the corrosion normally associated with the use of antifreeze mixtures. The all-around corrosion protection against aluminum, brass, solder, copper and iron shown by antifreeze D, which contains the preferred sperm oil-Ethylac oil phase is particularly striking.

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.

We claim:

1. An antifreeze mixture adapted to be added to water consisting essentially of a polyhydroxy alcohol freezing point depressant and 0.05–2% by volume of an insoluble oil phase inhibitor consisting essentially of a high boiling hydrocarbon oil and 0.5 to 5% by weight of 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide.

2. An antifreeze mixture of the type described in claim 1 in which the oil phase inhibitor consists essentially of 95 to 99.5 weight percent hydrocarbon oil and 0.5 to 5 percent 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide.

3. An antifreeze mixture adapted to be added to water consisting essentially of a polyhydroxy alcohol freezing point depressant and 0.5 to 2% by volume of said alcohol of an insoluble oil phase inhibitor consisting essentially of a high boiling hydrocarbon oil, 20–60% by weight of

sperm oil and 0.5–5% by weight of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide.

4. An antifreeze mixture of the type described in claim 3 in which the oil phase inhibitor consists essentially of hydrocarbon oil, 0.5% by weight of 2-benzothiazyl-N, N-diethylthiocarbamyl sulfide and 20 to 60% by weight of sperm oil.

5. An antifreeze mixture of the type described in claim 3 in which the oil phase inhibitor consists essentially of 54.5 weight percent naphthene base lube oil, 45 percent sperm oil and 0.5 percent 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide.

6. An antifreeze mixture adapted to be added to water consisting essentially of a polyhydroxy alcohol freezing point depressant containing a mixture of calcium hydroxide and boric acid, and 0.05 to 2% by volume based on said depressant of an insoluble oil phase inhibitor consisting essentially of 54.5 weight percent naphthene base lube oil, 45 percent sperm oil and 0.5 percent 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide.

7. A method for preparing an anti-freeze mixture adapted to be added to water comprising dissolving in a high boiling hydrocarbon oil the compound 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide in an amount sufficient to form a solution containing from 0.5 to 5% of said compound by weight, and then adding said hydrocarbon oil solution to a polyhydroxy alcohol freezing point depressant in an amount sufficient to form an anti-freeze mixture containing between 0.05 and 2% by volume of said oil solution.

8. A method in accordance with claim 7, also comprising adding sperm oil to said hydrocarbon oil and said compound to form a solution consisting essentially of hydrocarbon oil, 0.5 to 5% by said 2-benzothiazyl-N, N-dialkylthiocarbamyl sulfide and 20 to 60% by weight of sperm oil.

9. An antifreeze mixture adapted to be added to water consisting essentially of ethylene glycol and supernatant thereon from 0.05 to 2 volume % based on said ethylene glycol of an insoluble oil phase inhibitor consisting essentially of a high boiling hydrocarbon oil, 20 to 60% sperm oil and 0.5 to 5% of 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide.

10. An aqueous coolant consisting essentially of water, ethylene glycol, corrosion inhibiting amounts of calcium borate and 0.05 to 2% by volume based on said glycol of an insoluble oil phase corrosion inhibitor consisting essentially of 0.5 to 5% by weight of 2-benzothiazyl-N, N-diethylthiocarbamyl sulfide, balance a hydrocarbon oil.

11. An aqueous coolant comprising water, a polyhydroxy alcohol freezing point depressant and 0.05 to 2% by volume based on said alcohol of an oil phase corrosion inhibitor consisting essentially of a hydrocarbon oil and 0.5 to 5% by weight of said inhibitor of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide.

12. An aqueous coolant comprising water, a polyhydroxy alcohol freezing point depressant and 0.05 to 2% by volume based on said alcohol of an oil phase corrosion inhibitor consisting essentially of 0.5 to 5% by weight of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide, 20 to 60% by weight sperm oil, balance a hydrocarbon oil.

13. A permanent type antifreeze mixture consisting essentially of an ethylene glycol and 0.05 to 2% by volume of an insoluble oil phase inhibitor consisting essentially of 0.5 to 5% by weight of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide, balance a high boiling hydrocarbon oil.

14. An antifreeze composition consisting essentially of a polyhydric alcohol freezing point depressant containing corrosion inhibiting amounts of a salt selected from the group consisting of alkaline earth metal borates, alkali metal phosphates and alkali metal silicates and 0.05 to 2% by volume of an oil phase corrosion inhibitor consisting essentially of 0.5 to 5% by weight of 2-benzothiazyl-N,N-dialkylthiocarbamyl sulfide, balance a hydrocarbon oil.

References Cited in the file of this patent

UNITED STATES PATENTS

1,970,564	Hoover	Aug. 21, 1934
2,218,283	Fuller	Oct. 15, 1940
2,305,228	Woodhouse	Dec. 15, 1942
2,385,964	Bergen	Oct. 2, 1945
2,615,893	Hardman	Oct. 28, 1952

OTHER REFERENCES

I. and E. Chem.: vol. 40, page 2343 December 1948.