

UNITED STATES PATENT OFFICE

2,692,860

ANTIFREEZE COMPOSITIONS

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No Drawing. Application October 20, 1950,
Serial No. 191,327

2 Claims. (Cl. 252-75)

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This invention relates to compositions for use in the cooling system of an internal combustion engine and, more particularly, to antifreeze compositions the aqueous solutions of which when introduced into the lubricating system of the engine have no deleterious effect on the performance of the engine.

Alcohols have been widely used as freezing point depressants in the cooling systems of internal combustion engines. The dihydroxy alcohols such as ethylene glycol, propylene glycol, dipropylene glycol, diethylene glycol, and the like, because of their relatively high boiling points have been preferred over the more volatile monohydroxy alcohols such as methanol, ethanol, and propanol. This invention is therefore concerned with dihydroxy alcohol antifreeze compositions commonly referred to as "permanent type" antifreeze compositions.

Unfortunately, aqueous solutions of the dihydroxy alcohols have a corrosive action towards the ferrous and nonferrous metals encountered in the engine cooling systems. Many substances have heretofore been disclosed for inhibiting the corrosive action of aqueous dihydroxy alcohol antifreeze solutions but these substances for one or more reasons have not been entirely satisfactory.

Dihydroxy alcohol antifreeze compositions have been developed which give satisfactory protection against corrosion, but these compositions have not been entirely satisfactory in that it has been found that aqueous solutions of these compositions cause engine failure when they accidentally contaminate the oil of the lubricating system.

Engine failure in such a case is caused by the "freezing" or seizure of pistons, wrist pins, and other bearing surfaces. In the past, engine failure caused by the seizure of moving parts has been thought to be the result of employing a faulty lubricating oil. However, it has been found that the "freezing" of the moving parts is, so far as known, the result of a lubricating oil being contaminated with an aqueous solution of conventional "permanent type" antifreeze compositions. When such an aqueous antifreeze composition contaminates the lubricating oil, it has been found that oil-insoluble materials are formed and that these materials gradually build up on the surfaces of the moving parts. Since the clearances between pistons and cylinder walls, wrist pins and bushings, and bearings and bearing surfaces, are quite small, any build-up on the surfaces impairs lubrication. Accord-

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ingly, when the build-up of materials becomes so great that the clearance between the moving parts approaches zero, lubrication fails and "freezing" of the moving parts occurs.

Ordinarily, antifreeze compositions in the cooling system of internal combustion engine do not come in contact with the lubricating oil. Contamination of the oil with fluid from the cooling system may occur, however, as a result of a defective gasket or a cracked engine block.

It is therefore an object achieved by this invention to provide a "permanent type" dihydroxy alcohol antifreeze composition which not only prevents corrosion of metals in contact with aqueous solutions thereof but also avoids the freezing of pistons, wrist pins, and other bearing surfaces lubricated with an oil containing a portion of the aqueous antifreeze composition as a contaminant.

I have found that by incorporating a small amount of an alkali metal nitrite, an alkali metal salt of mercaptobenzothiazole, and an amine selected from the group consisting of aliphatic, alicyclic, and heterocyclic amines in a dihydroxy alcohol, not only the corrosion of metal parts in contact with aqueous solutions thereof is prevented, but also the seizure of moving parts lubricated with an oil contaminated with aqueous solutions thereof is avoided. The term "dihydroxy alcohol" as used herein and in the appended claims, includes the glycols, such as, for example, ethylene glycol, propylene glycol, dipropylene glycol, diethylene glycol, and mixtures containing them in predominating amounts.

The alkali metal nitrite in accordance with my invention is used in an amount between about 0.1 and 2.0 per cent by weight, based on the weight of the total composition. Particularly good corrosion inhibition is obtained with respect to ferrous metals when the alkali metal nitrite such as sodium or potassium nitrite is employed in an amount corresponding to about 0.5 per cent by weight. While alkali metal nitrites inhibit to a great extent the corrosion of ferrous metals caused by aqueous solutions of dihydroxy alcohols, these nitrites promote the corrosion of non-ferrous metals.

I have found that the corrosion of the nonferrous metals can be overcome and that the corrosion of ferrous metals can be further inhibited by employing a small amount of an aliphatic, alicyclic, or heterocyclic amine which may contain one or more hydroxyl groups, in conjunction with the nitrite, this despite the fact that

cyclohexylamine, for example, ordinarily promotes the corrosion of ferrous metals.

The aliphatic, alicyclic, and heterocyclic amines which are used in inhibiting the corrosion of ferrous and nonferrous metals when combined with an alkali metal nitrite are those having a boiling point between about 70° and about 280° C. The amines boiling above about 100° C. are preferred because there is less tendency of their being volatilized during use. Some of the amines which can be used are triethylamine, di-n-propylamine, tri-n-propylamine, n-butylamine, n-amylamine, di-n-amylamine, n-hexylamine, ethylene diamine, propylene diamine, ethanolamine, diethanolamine, triethanolamine, cyclohexylamine, dicyclohexylamine, ethyl hexylamine, N-ethyl aniline, morpholine ethanol, 1-(N-methyl)-amino hexane-2,3,4,5,6-pentol, and mixtures of mono- and di-n-alkylamines. A commercial mixture of amyl amines consisting of about 60 per cent mono-n-amylamine and about 40 per cent di-n-amylamine has given particularly good results. In accordance with my invention, the amine is used in an amount between about 0.1 and 2.0 per cent by weight based on the weight of the total composition. More than 2.0 per cent and as much as 5.0 per cent can be used without deleteriously affecting the beneficial properties of the other constituents. If less than about 0.1 per cent of amine is used, however, its corrosion inhibiting property with respect to nonferrous metals becomes ineffectual. In accordance with one embodiment of my invention, I employ cyclohexylamine in an amount corresponding to about 1.0 per cent by weight. In addition to the corrosion inhibiting properties given to the composition by the amine, the amine also supplies the composition with adequate reserve alkalinity.

A binary mixture of an alkali metal nitrite and an aliphatic, alicyclic, or heterocyclic amine in an aqueous dihydroxy alcohol solution greatly reduces the corrosion of ferrous and nonferrous metals found in the cooling system of an engine but this mixture tends to accelerate the corrosion of solder. Since the solder on the joints and seams of the cooling system is usually quite thin and the corrosion products of solder are voluminous, it is essential to inhibit the corrosion of solder in order to prevent the weakening and subsequential opening up of soldered seams and the plugging up of the radiator and cooling ducts in the engine block. I have found that a small amount of an alkali metal salt of mercaptobenzothiazole used in conjunction with the amine-nitrite mixture effectively inhibits corrosion of the solder without deleteriously affecting the beneficial corrosion inhibiting properties of either the amine or the nitrite.

In preparing the antifreeze composition of the present invention, the alkali metal salt of mercaptobenzothiazole may be added as such to the alcohol, or aqueous solutions of the alkali metal salt of mercaptobenzothiazole may be utilized, or mercaptobenzothiazole together with sufficient alkali metal hydroxide to make an alkaline solution may be used. In either case the net result is about the same in that the salt is readily hydrolyzed to mercaptobenzothiazole and an alkali metal hydroxide when the alcohol containing the salt or its aqueous solution is added to water. The alkali metal salt of mercaptobenzothiazole such as the sodium or potassium salt in accordance with my invention is employed in an amount between about 0.05 and 2.0 per cent

by weight based on the weight of the total composition. In accordance with a preferred embodiment of the invention, I employ 0.2 per cent by weight of a 45 to 50 per cent by weight aqueous solution of the sodium salt of mercaptobenzothiazole.

The total weight of the addition agents consisting of alkali metal nitrite, alkali metal salt of mercaptobenzothiazole and amine selected from the group consisting of aliphatic, alicyclic, and heterocyclic amines used with the dihydroxy alcohol will depend not only upon the particular alcohol employed but also upon the particular compounds chosen. In general, however, the addition agents will constitute about 0.25 to 6.0 per cent by weight of the antifreeze composition.

In preparing the antifreeze composition of the invention, the addition agents can be admixed with the alcohol in any convenient manner. The agents may be added separately or they may be blended together in the desired proportion to form an addend concentrate which can then be added to the alcohol. The antifreeze composition can then be diluted with water to any desired concentration. Ordinarily, glycols are diluted with water to a concentration of about 50 per cent by volume or less. The anti-corrosion and the anti-engine failure properties of the antifreeze compositions of the invention, however, are obtained at any reasonable degree of aqueous dilution.

The advantages to be obtained by the use of the antifreeze compositions of the present invention as compared with similar compositions containing only one or two of the three addition agents are illustrated by a test which consists of immersing clean weighed metal specimens in sufficient aqueous antifreeze solution to give a solution to metal surface ratio of about 8 milliliters of solution per square inch of metal surface. The solution containing the metal specimen is maintained at 160° F. and is constantly agitated by bubbling air through the solution for 336 hours. The corrosion inhibiting properties of the solution are then evaluated by visual inspection of the surface of the metal specimen and by determining its weight loss. Any change in the concentration of the hydrogen ion content of the solution is determined by measuring its pH before and after the 336 hour test period.

Comparative corrosion test results for an aqueous antifreeze solution containing 20 per cent by volume of ethylene glycol and the indicated addition agents are given in the following Table 1. The indicated amounts of the addition agents are expressed as per cent by weight based upon the weight of the ethylene glycol. In preparing the test solutions, the addition agent was first added to the ethylene glycol. The ethylene glycol containing the addition agent was then diluted to 20 per cent concentration with water. The corrosion data are expressed in milligrams of metal lost per square inch of surface area exposed per 336 hours of exposure. The metal specimens used in conducting the corrosion tests were metal couples made by offsetting

$$1\frac{3}{8}'' \times 1'' \times \frac{1}{8}''$$

strips of electrolytic copper and SAE 1020 steel by $\frac{5}{8}''$ in the lengthwise direction and filling in the offsets with solder in a manner to give a $\frac{5}{8}'' \times 1'' \times \frac{1}{8}''$ solder block at each end of the specimens. The resulting copper-steel-solder couples thus obtained measured $2'' \times 1'' \times \frac{1}{4}''$.

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Table 1

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Test No.	Addition Agent	Corrosion Loss, mg./sq. in./336 hrs.	pH Before Test	pH After Test
1	None	140.4	7.48	5.02
2	Cyclohexylamine, 1%	517.0	10.03	4.39
3	Sodium mercaptobenzothiazole (50% solution), 0.2%	193.0	8.02	4.40
4	Sodium nitrite, 0.5%	42.3	7.50	9.61
5	Cyclohexylamine, 1%	154.0	11.06	4.38
6	Sodium mercaptobenzothiazole (50% solution), 0.2%	10.8	10.98	8.67
7	Sodium nitrite, 0.5%	33.2	7.98	9.65
8	Cyclohexylamine, 1%	8.9	10.96	9.67
	Sodium mercaptobenzothiazole (50% solution), 0.2%			
	Sodium nitrite, 0.5%			

Visual inspection of the metal specimens in contact with the solutions listed above showed that the steel strips in tests Nos. 1, 2, 3 and 5 were badly corroded. However, the copper and solder in tests Nos. 1, 2, 3 and 5 were not attacked. The corrosion of the steel in test No. 4 when utilizing sodium nitrite in the aqueous ethylene glycol solution was considerably less than the corrosion caused by the aqueous solution of ethylene glycol alone, but in this case the copper was slightly corroded. However, the solder was not attacked in test No. 4. In test No. 6 the utilization of cyclohexylamine in combination with sodium nitrite improved the corrosion inhibiting characteristics of the aqueous solution of ethylene glycol toward steel and copper, but in this case the solder was etched. By replacing the cyclohexylamine of test No. 6 with sodium mercaptobenzothiazole in accordance with test No. 7, the corrosion of the solder and copper was inhibited but the steel was corroded more than it had been in test No. 6. Optimum protection against corrosion of the steel, copper and solder was obtained in test No. 8. In test No. 8 the antifreeze composition corresponded to a composition of the invention.

When the tests reported in Table 1 were repeated employing a 50 per cent (by volume) aqueous solution of ethylene glycol, comparable results were obtained.

In order to illustrate the protection afforded single metals in contact with a 50 per cent (by volume) aqueous solution of the antifreeze compositions of the invention, 1" x 2" x $\frac{1}{8}$ " strips of cast iron and cast aluminum and 1" x 2" x $\frac{1}{2}$ " strips of electrolytic copper were subjected to the test described above. The test results for both inhibited and uninhibited aqueous solutions of ethylene glycol and for water are given in Table 2.

Table 2

Solution	Metal	Corrosion Loss, mg./sq. in./336 hrs.	pH Before Test	pH After Test
Tap Water	Iron	206.6	7.49	8.18
	Copper	1.3	7.49	7.71
	Aluminum	3.5	7.49	8.08
50% Aqueous Solution of Ethylene Glycol	Iron	178.6	5.52	4.98
	Copper	7.5	5.52	5.17
	Aluminum	0.9	5.52	6.69
50% Aqueous Solution of Ethylene Glycol containing 2% by weight of cyclohexylamine, 0.5% sodium nitrite, and 0.2% sodium mercaptobenzothiazole (50% solution).	Iron	0.1	10.86	8.71
	Copper	1.9	10.86	8.18
	Aluminum	1.8	10.86	8.46

It will be noted that water and aqueous ethylene glycol caused severe corrosion of iron but that an aqueous solution of an antifreeze composition of the invention caused substantially no corrosion of iron. It will be noted further that the aqueous solution containing the antifreeze composition of the invention gave adequate protection to copper and aluminum.

In addition to preventing the corrosion of metal in the cooling system of an engine, the compositions of the present invention have the important property not possessed by conventional compositions of preventing engine failure when a portion of the aqueous antifreeze composition leaks into the lubricating system. In order to illustrate the latter property of the composition of the invention and to compare this composition with antifreeze compositions containing borax, a single-cylinder Lauson model LF822 engine equipped with a special cylinder head and loaded by means of a 3 horsepower, 1700 R. P. M., 3 phase induction motor, was used. An auxiliary oil sump was installed between the engine sump and cylinder in order to operate the engine with a 0.35 pound oil charge. A small adjustable orifice was installed between the combustion chamber and the coolant passages in the cylinder head. During operation the orifice was adjusted to permit a constant flow of exhaust gases to pass through the antifreeze coolant.

With the coolant temperature maintained at 140° F. maximum, the engine was run at 1000 R. P. M. idle for 10 minutes, under load at $\frac{1}{2}$ throttle opening for 30 minutes, and at 1000 R. P. M. idle for 10 minutes. A portion of the antifreeze coolant was then permitted to drip into the cylinder at the rate of three drops a minute for three hours while the piston was at bottom dead center after the compression stroke. The entire above operation was repeated 10 times, after which the engine was run for 10 minutes at 1000 R. P. M. idle and then for 60 minutes under load at full throttle. During the 60 minute run the coolant temperature was held at 190° F. The above procedure constituted one cycle. If no indication of engine malfunction was noted, the cycle was repeated six times or until operational failure, which constitutes freezing of either the wrist pin or the piston.

The results of the Lauson engine test are given in the following Table 3. In the table, antifreeze A and antifreeze B are commercially marketed permanent type antifreeze compositions containing, respectively, about 1.5 and 2.0 per cent of borax. Antifreeze C was a composition of the invention consisting of 98.3 per cent ethylene glycol, 1 per cent cyclohexylamine, 0.5 per cent sodium nitrite, and 0.2 per cent of sodium mercaptobenzothiazole (50 per cent solution).

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Table 3

Coolant	Lauson En- gine Test Cycles
50% Aqueous Solution of Antifreeze A-----	2.2
50% Aqueous Solution of Antifreeze B-----	1.8
50% Aqueous Solution of Antifreeze C-----	6

Upon examination of the engines in which the aqueous solutions of antifreeze A and antifreeze B had been introduced, it was found that in each instance the wrist pins had frozen in both rod and piston. Also, there was a heavy deposit on the pistons and cylinder walls. Examination of the engine in which the aqueous solution of the composition of the invention had been introduced showed that the bearing surfaces were in excellent condition.

While the invention has been described herein with particular reference to certain specific embodiments thereof by way of illustration, it is to be understood that the invention is not limited to such embodiments except as hereinafter defined in the appended claims.

I claim:

1. A permanent type antifreeze composition

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consisting essentially of ethylene glycol, about 0.5 per cent by weight of sodium nitrite, about 0.2 per cent by weight of a 50 per cent aqueous solution of sodium mercaptobenzothiazole, and about 1.0 per cent by weight of cyclohexylamine.

2. A permanent type antifreeze composition consisting essentially of a lower dihydroxy alcohol, about 0.5 per cent by weight of sodium nitrite, about 0.2 per cent by weight of a 50 per cent aqueous solution of sodium mercaptobenzothiazole, and about 1.0 per cent by weight of cyclohexylamine.

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