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LUBRICATING COMPOSITIONS CONTAINING 2-BENZOTHIAZYL - N,N - DIALKYLDITHIOCARBAMATES

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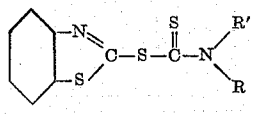
21 Claims. (Cl. 252—33.4)

This invention relates to hydrocarbon oil compositions having improved anti-corrosive properties. More particularly it relates to lubricating oil compositions containing small amounts of 2-benzothiazyl-N,N-dialkyldithiocarbamates.

Metals in prolonged contact with hydrocarbon oils ordinarily undergo considerable corrosion due to the insufficient protection which such oils afford metals against the action of oxygen or water or of corrosive compounds contained in the oils themselves. This is especially true in the case of petroleum products, which tend to undergo oxidation in the presence of air with the formation of acidic compounds and in which corrosive sulfur-containing compounds may be either originally present or introduced during the refining process. It is, therefore, common practice to add to lubricating and preservative oils various types of compounds for imparting anticorrosiveness, particularly to ferrous metals and copper. A large number of different compounds have been employed for this purpose, one of the most effective being 2-mercaptobenzothiazole, which functions both as a corrosion inhibitor and as an antioxidant. However the compounds which have been employed heretofore are not sufficiently effective to impart the degree of anticorrosiveness required in many cases, and the effect obtainable by 2-mercaptobenzothiadole, for example, is furthermore limited by the slight solubility of the compound in hydrocarbon oils.

A principal object of the present invention is to provide an improved lubricating oil having excellent anticorrosive properties. Another object is to provide an improved hydraulic oil capable of meeting the rigorous specification requirements for aircraft hydraulic oils. Still another object is to provide an improved lubricating and preservative oil which affords prolonged protection against metal corrosion in damp or humid atmospheres.

In accordance with our invention a hydrocarbon oil composition having greatly improved corrosion inhibiting properties in contact with metals is obtained by adding to such composition a small amount of a 2-benzothiazyl-N,N-dialkyldithiocarbamate. Compounds of this class may be represented by the following formula



wherein R and R′ are alkyl groups which may be the same or different, having from one up to about fifteen carbon atoms, or higher, and preferably from one to about

six carbon atoms. Examples of such compounds which may be mentioned include 2-benzothiazyl-N,N-ditertiarybutyldithiocarbamate, 2-benzothiazyl-N,N - ethylhexyldithiocarbamate, 2-benzothiazyl-N,N-methylisopropyldithiocarbamate, 2-benzothiazyl-N,N-diamyldithiocarbamate, and so forth. A very suitable compound of this type, for example, is 2-benzothiazyl-N,N-diethyldithiocarbamate. This compound is commercially available under the trade name of "Ethylac."

We have found that hydrocarbon oil compositions containing small amounts of the above compounds have greatly improved anticorrosiveness to metals, particularly to ferrous metals and copper, as compared with such compositions containing other anticorrosive agents heretofore employed for this purpose. In comparison with the widely used compound 2-mercaptobenzothiazole, for example, they impart superior anticorrosiveness and equivalent oxidation stability to the compositions. In addition they have greatly improved solubility and chemical stability.

These compounds impart improved anticorrosiveness to hydrocarbon oils even when present in small amounts. In lubricating and preservative oils they are preferably employed in amounts between about 0.005 to about 0.2 percent by weight, although somewhat smaller or larger amounts up to their limit of solubility may be employed if desired.

Lubricating oils containing these compounds may also contain other additives of the usual types so far as no incompatibility exists, as for example anti-wear agents, viscosity improvers, oxidation inhibitors, other corrosion inhibitors, and so forth, as well as metal soaps or other thickening agents either in minor amounts or in grease forming proportions.

The anticorrosive properties of hydrocarbon oils containing 2-benzothiazyl-N,N-dialkyldithiocarbamates has been demonstrated by adding a typical compound of this class, 2-benzothiazyl-N,N-diethyldithiocarbamate, to a number of different hydrocarbon oils and determining the corrosiveness of the resulting compositions to metals by means of standard tests. While 2-benzothiazyl-N,N-diethyldithiocarbamate has been used in the following examples for purposes of illustration, it is to be understood that any of the compounds of this class described above may be used if desired.

In accordance with our invention a superior hydraulic oil having a high degree of anticorrosiveness to metals was developed by the addition of 2-benzothiazyl-N,N-diethyldithiocarbamate to a base oil containing other additives for imparting oxidation stability, viscosity improvement and anti-wear properties to the composition. The base oil employed was a solvent refined naphthenic oil having an API gravity of 35°, a flash point, COC, of 210° F., a kinematic viscosity at 100° F. of 3.48 and a neutralization number of 0.01. A composition comprising a mixture of methyl and ethyl methacrylate polymers in the form of a 50% concentrate in a white oil was added to this base oil to improve viscosity characteristics. Tricresyl phosphate was also added as an anti-wear agent. To this composition various corrosion and oxidation inhibitors were added, including 2-benzothiazyl-N,N-diethyldithiocarbamate, and the corrosiveness of the resulting compositions determined. The results are given in Table I below.

TABLE I

Hydraulic oils

OXIDATION-CORROSION STABILITY TEST

Oil No.	1	2	3	4	5	6	7	8
Composition:								
Hydraulic base oil	85.56	85.56	85.62	85.62	85.62	85.52	85.32	85.32.
Methacrylate polymer concentrate	13.62	13.62	13.62	13.62	13.62	13.62	13.62	13.62.
Tricresyl phosphate	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50.
4-Methyl-2,6-ditertiarybutyl phenol	0.30	0.30					0.30	0.30.
Zinc dibutyldithiocarbamate			0.25	0.25	0.25	0.25	0.25	0.25.
2-Mercaptobenzothiazole	0.01			0.01			0.01	
2-Benzothiazyl-N,N-diethyldithiocarbamate.		0.01			0.01	0.10		0.01.
Metal Wt. Change, mg./sq. cm.:								
Fe	−0.07	0.00	−0.01	0.00	0.00	0.00	+0.01	+0.01.
Al	−0.03	+0.01	−0.01	−0.03	−0.01	+0.01	+0.01	0.00.
Mg	−0.03	+0.01	0.00	−0.03	0.00	0.00	−0.01	−0.02.
Cu	−0.38	−0.18	−0.52	−0.15	−0.03	0.00	−0.15	−0.04.
Cd	−0.03	−0.04	−0.02	0.00	0.00	−0.02	0.00	0.00.
Metal Appearance:								
Fe	Small Stain	One Stain	Clean	Clean	Clean	Clean	Clean	Clean.
Al	do	Clean	do	do	do	do	do	Do.
Mg	Clean	do	do	do	do	do	do	Do.
Cu	Dull, border line.	Dull, slight peacock.	Stained	Dull	do	do	Pitted	Do.
Cd	Slightly grey	Clean	Clean	Clean	do	do	Clean	Do.
Used Oil Tests:								
Neut. No. Rise	0.00	0.00	0.20	0.02	0.00	0.03	0.00	0.03.
Appearance	Original	Original	Dark	Slightly dark-ened.	Original	Original	Dark	Slightly dark-ened.

The oxidation and corrosion stability test of the foregoing table is that prescribed in specification MIL–O–5606 for aircraft hydraulic fluids and is carried out in the following manner: 100 cc. of the oil under test are placed in a large test tube fitted with a reflux condenser and immersed in a bath maintained at 121.1° C. Weighed metal strips, one of copper, one of low carbon, non-carbon-bearing steel, one of aluminum alloy, one of magnesium alloy and one of cadmium plated steel, each about 1 inch square, are fastened together so that the magnesium and copper do not touch and placed in the test oil. Dry air is bubbled through the oil at a rate of approximately 5 liters per hour during the test. At the end of 168 hours, the test is discontinued, the neutralization number of the oil determined, and the metal test specimens examined and reweighed to determine the loss due to corrosion.

The data given in Table I show that 2-benzothiazyl-N,N-diethyldithiocarbamate imparted superior anticorrosiveness and equal oxidation resistance as compared with equal amounts of 2-mercaptobenzothiazole to a medium viscosity oil containing other inhibitors of the types commonly employed in such oils. Furthermore the 2-benzothiazyl-N,N-diethyldithiocarbamate was found to be entirely compatible with these other inhibitors either singly or in combinations, indicating that oils may be produced by use of the inhibitors of our invention having a superior tolerance of contamination with most commercial lubricating or hydraulic oils. As shown by Table I, oils having outstandingly superior oxidation-corrosion stability characteristics were obtained by use of the inhibitor combination comprising 2-benzothiazyl-N,N-diethyldithiocarbamate and zinc dibutyldithiocarbamate. No deterioration in these properties resulted when 4-methyl-2,6-ditertiary-butyl phenol was added as a third component of the inhibitor combination. Considerably less improvement in anticorrosiveness was obtained by the use of inhibitor combinations comprising zinc dibutyldithiocarbamate or 4-methyl-2,6-ditertiary-butyl phenol with 2-mercaptobenzothiazole instead of 2-benzothiazyl-N,N-diethyldithiocarbamate, while an inhibitor combination comprising 2-mercaptobenzothiazole with both zinc dibutyldithiocarbamate and 4-methyl-2,6-ditertiary-butyl phenol produced an oil which failed to meet the MIL–O–5606 oxidation-corrosion stability specifications.

In addition to the superior effectiveness of 2-benzothiazyl-N,N-diethyldithiocarbamate as compared with 2-mercaptobenzothiazole on an equal weight basis, it is possible to employ larger amounts of the former to obtain still further effect because of its higher solubility, amounting to at least 0.1 percent by weight in a medium viscosity oil as compared with about 0.01 percent by weight for 2-mercaptobenzothiazole. Table II below shows the relative solubilities of these two compounds in the hydraulic base oil employed in the oils of Table I. In making these measurements the inhibitor was dissolved in the oil by heating the oil at 190° F. and stirring for one hour. As soon as the solution had cooled to room temperature the turbidity was measured by means of a potentiometer type photoelectric photometer, which is sold under the trade name of "Lumetron."

TABLE II

Relative oil solubilities of 2-benzothiazyl-N,N-diethyldithiocarbamate and 2-mercaptobenzothiazole

Additive Content, Wt. Percent	0.01	0.03	0.05	0.07	0.09	0.10
2 - Benzothiazyl - N,N - diethyldithiocarbamate:						
Cold appearance	Clear	Clear	Clear	Clear	Clear	Clear.[1]
Lumetron turbidity, percent Transmission.	97	97	100	98	98	96.
2-Mercaptobenzothiazole:						
Cold appearance	Clear	Slightly Hazy				Opaque.[2]
Lumetron turbidity, percent Transmission.	89	77				23.

[1] Remained clear indefinitely.
[2] Upon standing for 2 days, much of the additive settled out and large, needle-like crystals formed.

naphthalene, such as other alkylated aromatic compounds or compounds of different types, as for example ethylene glycol distearate or sweatings from oxidized paraffin wax. The above additives may be present in varying amounts according to the effects to be produced, suitably 0.1–1.0 percent by weight of the phenolic oxidation inhibitor, about 1–10 percent by weight of the sulfonate and about 0.05–1.0 percent by weight of the pour depressant, although larger or smaller amounts may be employed if desired.

While the above examples serve to illustrate typical compositions employing our novel corrosion inhibitors, it is understood that the invention is not to be limited thereto. It will be evident from the above that they may be employed equally well in other lubricating oil compositions, such as cutting oils, turbine oils, and so forth.

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. A hydrocarbon lubricating oil containing a corrosion inhibiting amount of a 2-benzothiazyl-N,N-dialkyldithiocarbamate.

2. A mineral lubricating oil containing a corrosion inhibiting amount of 2-benzothiazyl-N,N-dialkyldithiocarbamate.

3. A mineral lubricating oil containing from about 0.005 to about 0.2 percent by weight of 2-benzothiazyl-N,N-diethyldithiocarbamate.

4. A hydraulic oil comprising in major proportion a mineral lubricating base oil compounded with about 0.1–1.0 percent by weight of a polyvalent metal salt of a dialkyldithiocarbamic acid, and about 0.005–0.2 percent by weight of 2-benzothiazyl-N,N-dialkyldithiocarbamate.

5. A hydraulic oil according to claim 4 wherein the polyvalent metal salt is zinc dibutyldithiocarbamate.

6. A hydraulic oil according to claim 5 wherein the 2-benzothiazyl-N,N-dialkyldithiocarbamate is 2-benzothiazyl-N,N-diethyldithiocarbamate.

7. A hydraulic oil having substantially the following composition in percentages by weight:

Phosphorus acid ester	0.1–1.0
Polyvalent metal dialkyldithiocarbamate	0.005–0.2
2-benzothiazyl - N,N-dialkyldithiocarbamate	0.005–0.2
Methacrylate ester polymer	1–15
Mineral lubricating oil	Balance

8. A hydraulic oil having substantially the following composition in percentages by weight:

Tricresyl phosphate	0.1–1.0
Zinc dibutyldithiocarbamate	0.1–0.5
2-benzothiazyl-N,N-diethyldithiocarbamate	0.01–0.2
Methacrylate ester polymer	3–10
Mineral lubricating oil	Balance

9. A lubricating and rust preventive composition comprising in major proportion a mineral lubricating base oil compounded with about 1–10 percent by weight of an oil-soluble petroleum sulfonate, and about 0.005–0.2 percent by weight of 2-benzothiazyl-N,N-dialkyldithiocarbamate.

10. A lubricating and rust preventive composition according to claim 9, also containing 0.1–1.0 percent by weight of a phenolic oxidation inhibitor.

11. A composition comprising in major proportion a mineral lubricating base oil compounded with about 0.1–1.0 percent by weight of 4-methyl-2,6-ditertiary butyl phenol, and about 0.005–0.1 percent by weight of 2-benzothiazyl-N,N-dialkyldithiocarbamate.

12. A lubricating and rust preventive oil having substantially the following composition in percentages by weight:

Oil-soluble petroleum sulfonate	1–10
Phenolic oxidation inhibitor	0.1–1.0
Alkylated aromatic pour depressant compound	0.05–1.0
2-benzothiazyl-N,N-dialkyldithiocarbamate	0.005–0.1
Mineral lubricating oil	Balance

13. A lubricating and rust preventive oil having substantially the following composition in percentages by weight:

Calcium mahogany sulfonate	1–10
4-methyl-2,6-ditertiarybutylphenol	0.1–1.0
Naphthalene - chlorinated wax condensation product	0.05–1.0
2-benzothiazyl-N,N-diethyldithiocarbamate	0.005–0.1
Mineral lubricating oil	Balance

14. A mineral lubricating oil containing a corrosion inhibiting amount of a 2-benzothiazyl-N,N-dialkyldithiocarbamate wherein each of the said alkyl groups contains from 1 to 6 carbon atoms.

15. A lubricating oil composition comprising in major proportion a mineral lubricating base oil compounded with about 0.1–1.0 percent by weight of a polyvalent metal salt of a dialkyldithiocarbamic acid, and about 0.005–0.2 percent by weight of a 2-benzothiazyl-N,N-dialkyldithiocarbamate wherein each of the said alkyl groups contains from 1 to 6 carbon atoms.

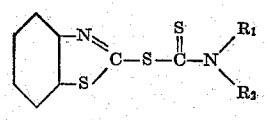
16. A lubricating oil composition comprising in major proportion a mineral lubricating base oil compounded with about 0.1–1.0 percent by weight of a phosphorus acid ester, about 0.005–0.2 percent by weight of a polyvalent metal dialkyldithiocarbamate, and about 0.005–0.2 percent by weight of a 2-benzothiazyl-N,N-dialkyldithiocarbamate wherein each of the said alkyl groups contains from 1 to 6 carbon atoms.

17. A lubricating oil composition comprising in major proportion a mineral lubricating base oil compounded with about 1–10 percent by weight of an oil-soluble petroleum sulfonate, and about 0.005–0.2 percent by weight of a 2-benzothiazyl-N,N-dialkyldithiocarbamate wherein each of the said alkyl groups contains from 1 to 6 carbon atoms.

18. A composition comprising in major proportion a mineral lubricating base oil compounded with about 0.1–1.0 percent by weight of a phenolic oxidation inhibitor and about 0.005–0.1 percent by weight of a 2-benzothiazyl-N,N-dialkyldithiocarbamate wherein each of the said alkyl groups contains from 1 to 6 carbon atoms.

19. A lubricating oil composition comprising in major proportion a mineral lubricating base oil compounded with about 1–10 percent by weight of an oil-soluble petroleum sulfonate, about 0.1–1.0 percent by weight of a phenolic oxidation inhibitor and about 0.005–0.1 percent by weight of a 2-benzothiazyl-N,N-dialkyldithiocarbamate wherein each of the said alkyl groups contains from 1 to 6 carbon atoms.

20. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and a corrosion inhibiting proportion of a compound having the formula:



in which R_1 and R_2 are alkyl radicals having from 2 to 5 carbon atoms.

21. A lubricating oil composition comprising a major

In place of the base oil employed in the above hydraulic oil compositions, other suitable lubricating oils may be employed, such as different mineral oil fractions obtained from different types of crude oils or produced by different refining methods, synthetic oils, and so forth. Furthermore, in place of or in addition to the other additives employed in combination with the inhibitors of our invention, compounds of similar nature or their recognized equivalents may be used. Thus, in place of 4-methyl-2,6-ditertiary-butyl phenol, compositions of the above type may contain other phenolic oxidation inhibitors, particularly the tri-alkylated phenols containing sufficient alkyl carbon atoms to promote oil solubility, such as for example 2,4,6-tritertiary-butyl phenol, 2-isopropyl-4,6-dimethyl phenol and 2,6-ditertiary-butyl-4-tertiary-amyl phenol. In place of zinc dibutyldithiocarbamate, these compositions may contain other compounds of the class comprising metal salts of dialkyldithiocarbamic acids, as disclosed for example by Denison et al., U. S. Patent 2,394,536. Salts of a dialkyldithiocarbamic acid with a polyvalent metal such as calcium or zinc are preferred for this purpose. These are suitably employed in amounts ranging from about 0.1 to 1.0 percent by weight. The tricresyl phosphate may be substituted by another suitable ester of phosphoric or phosphorous acid or by a different type of anti-wear agent such as dibenzyl disulfide. Also, in place of the methacrylate polymer other suitable materials for improving the viscosity and viscosity index characteristics may be employed such as other polymeric materials or condensation products for example isobutylene polymer. The viscosity improvers are generally employed in a proportion of about 1–15% by weight (basis the polymer).

Still further in accordance with our invention a lubricating and preservative composition especially suitable as an aircraft instrument oil was developed by the use of 2-benzothiazyl-N,N-diethyldithiocarbamate in a medium viscosity oil. The base oil employed was a blend comprising 71 percent by weight of a highly sulfur dioxide refined naphthenic type distillate oil having an SUS viscosity at 100° F. of about 50 and 29 percent by weight of a sulfur dioxide refined naphthene base distillate oil having an SUS viscosity at 100° F. of about 100. Other additives were employed comprising a rust inhibitor, an oxidation inhibitor and a pour depressant, the latter being an alkylated naphthalene obtained by reacting naphthalene with chlorinated wax in the presence of aluminum chloride and commercially available under the trade name of "Paraflow." The finished oil had the following composition:

	Weight percent
Base oil	94.59
Calcium mahogany sulfonate	5.00
4-methyl-2,6-ditertiarybutyl phenol	0.30
Paraflow	0.10
2-benzothiazyl-N,N-diethyldithiocarbamate	0.01

The above oil very satisfactorily met all the requirements of Army-Navy specification AN–O–6a, Amendment–4 (February 19, 1948) for general purpose, low temperature lubricating oils. Table III below shows the corrosion and oxidation stability and the corrosion protection properties of this composition, designated oil No. 9, against the requirements of the said Army-Navy specification.

TABLE III

General purpose, low temperature lubricating oil

OXIDATION-CORROSION STABILITY AND CORROSION PREVENTION TESTS

	Oil No. 9	AN–O–6a Requirements
Corrosion:		
Change in Wt., mg./cm.²:		
Copper	−0.11	±0.2 Max.
Steel	−0.01	Do.
Aluminum Alloy	0.00	Do.
Magnesium alloy	0.00	Do.
Cadmium plated steel	−0.03	0.2.
Pitting, all metals	None	None.
Etching, all metals	do	Do.
Visible corrosion 20X, all metals.	do	Do.
Appearance	Brassy	Slight discoloration permissible.
Oxidation:		
Vis. change, C. S. at 100° F., percent of original.	+1	−5 to +20.
Neut. No. increase	0.02	0.20 Max.
Separation of insoluble materials.	None	None.
Gumming	do	Do.
Weight loss, percent	1	5 Max.
Corrosion Protection:		
Humidity Cabinet Test, hrs.	504 (clean) 528 (rust specks)	100 Min.

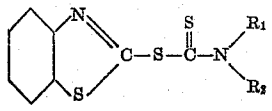
The oxidation and corrosion test results of the foregoing table were obtained by the oxidation and corrosion stability test as described in connection with Table I.

The humidity cabinet test of the foregoing table is a test for determining the amount of protection afforded to steel surfaces by an oil under rusting conditions. Two clean, non-copper-bearing steel panels, each two inches by four inches by ⅛ inch thick, are employed in this test. These are dipped in the test oil at room temperature (77° F.), allowed to drain for 2 hours at the same temperature and then suspended in a humidity cabinet maintained at 120° F. The air in the cabinet is saturated with water vapor at this temperature, so that continuous condensation occurs upon the panels. The panels are examined every 24 hours for evidence of corrosion. The oil is considered as having passed the test if, at the end of 100 hours neither of the panels shows more than a trace of corrosion, defined as not more than three small spots no one of which is more than one millimeter in diameter.

Table III shows that the corrosion inhibitors of our invention impart exceptional rust preventing properties in addition to excellent oxidation and corrosion stability properties to hydrocarbon oils. The superior effectiveness of these compounds in imparting anti-rusting properties to hydrocarbon oils is demonstrated by the fact that a composition identical with oil No. 9 of the above table with the exception that an equal weight of 2-mercaptobenzothiazole was substituted for the 2-benzothiazyl-N,N-diethyldithiocarbamate gave only 240 hours of protection in the humidity cabinet test.

In place of the oil base employed in oil No. 9 described above, other lubricating oil fractions may be employed as discussed in connection with the oils of Table I. Likewise other additives of similar function may be substituted for those employed in combination with the inhibitors of our invention. For example, in place of 4-methyl-2,6-ditertiary butyl phenol, other phenolic oxidation inhibitors may be employed as discussed above. In place of calcium mahogany sulfonate, other oil-soluble sulfonic acid salts may be employed which may be obtained from different sulfonic acids or by neutralizing sulfonic acids with suitable compounds of various other metals such as the oxides or hydroxides of sodium, potassium, ammonium, barium, aluminum, etc. Different pour depressors may also be employed in place of the alkylated

proportion of a mineral lubricating oil and a corrosion inhibiting proportion of a compound having the formula:



in which R_1 and R_2 are alkyl radicals.

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