United States Patent [19]

Malec

[11] **3,833,496**

[45] **Sept. 3, 1974**

[54] **OIL COMPOSITION**

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[73] Assignee: **Ethyl Corporation,** Richmond, Va.

[22] Filed: **Apr. 6, 1973**

[21] Appl. No.: **348,625**

[52] **U.S. Cl.**..... **252/33.6,** 252/47.5, 260/455 A

[51] **Int. Cl.** **C10m 1/38,** C10m 1/32

[58] **Field of Search**..... 252/34, 33.6, 47.5; 260/455 A

[56] **References Cited**

UNITED STATES PATENTS

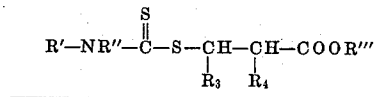
2,756,249	7/1956	Kirshenbaum et al.	252/47.5 X
2,897,152	7/1959	Elliott et al.	252/47.5 X

Primary Examiner—W. Cannon

Attorney, Agent, or Firm—Donald L. Johnson; Robert A. Linn; Joseph D. Odenweller

[57] **ABSTRACT**

Compounds having the formula:



wherein R′ is selected from the group consisting of aliphatic hydrocarbon radicals containing about 8–100 carbon atoms, and hydrocarbylaminohydrocarbyl radicals having the formula:

$$R_1\text{-}NR''''\text{-}R_2\text{-}$$

wherein R_1 is an aliphatic hydrocarbon radical containing about 8–100 carbon atoms, R′′′′ is selected from the group consisting of hydrogen and C_{1-4} alkyls and R_2 is a divalent aliphatic hydrocarbon radical containing about 2–10 carbon atoms, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals containing about 1–4 carbon atoms, R′′ is selected from the group consisting of hydrogen and C_{1-4} alkyls and R′′′ is selected from the group consisting of hydrogen, C_{1-10} alkyl and salt cations, are effective antiwear and antirust additives in lubricating oils and greases.

6 Claims, No Drawings

OIL COMPOSITION

BACKGROUND

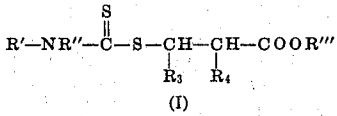
Additives are conventionally added to lubricating oil and grease to improve their properties. Antiwear additives used in the past include compounds such as zinc dialkyldithiophosphates, sulfurized sperm oil, and the like. Antirust protection can be provided by compounds such as overbased calcium sulfonates. Long chain amines such as polybutenyl ethylenediamine have been used to improve dispersancy of lubricating oils.

SUMMARY OF THE INVENTION

According to the present invention, lubricating oils and greases having improved antiwear and antirust properties are provided by including in the lubricating oil composition certain 3-mercaptoalkanoic acid, [(alkylamino)alkyl] dithio-carbamates such as 3-mercaptobutyric acid, [3(oleylamino)-propyl] dithiocarbamate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A preferred embodiment of the invention is an antiwear-antirust additive for lubricating oils and greases having the formula:



(I)

wherein R′ is selected from the group consisting of aliphatic hydrocarbon radicals containing about 8–100 carbon atoms, and hydrocarbylaminohydrocarbyl radicals having the formula:

$$R_1 - NR'''' - R_2 -$$

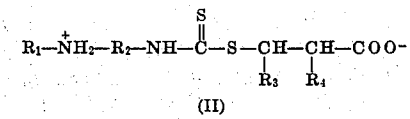
wherein R_1 is an aliphatic hydrocarbon radical containing about 8–100 carbon atoms, R′′′′ is selected from the group consisting of hydrogen and C_{1-4} alkyls and R_2 is a divalent aliphatic hydrocarbon radical containing about 2–10 carbon atoms, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals containing about 1–4 carbon atoms, R′′ is selected from the group consisting of hydrogen and C_{1-4} alkyls and R′′′ is selected from the group consisting of hydrogen, C_{1-10} alkyl and salt cations. Useful salt cations include the cations of the alkaline earth metals such as calcium, magnesium, strontium, and barium; ammonium ions formed from ammonia; alkyl and alkenyl amines such as methylamine, dimethylamine, trimethylamine, triethylamine, tributylamine, ethanolamine, diethanolamine, triethanolamine, morpholine, stearylamine, oleylamine, palmylamine, laurylamine, eicosylamine, eicosenylamine, and the like; and other metal cations such as zinc, aluminum, nickel, manganese, iron, and the like.

Representative examples of the above additives include:

3-mercaptopropionic acid, n-octyldithiocarbamate
3-mercaptobutyric acid, stearyldithiocarbamate
calcium 3-mercaptobutyrate, oleyldithiocarbamate
zinc 3-mercaptopropionate, palmyldithiocarbamate

trimethylammonium 3-mercaptohexanoate, C_{100}-polybutenyl dithiocarbamate
manganese 3-mercaptobutyrate, stearyldithiocarbamate
barium 3-mercaptoheptanoate, eicosyldithiocarbamate
magnesium 3-mercaptobutyrate, eicosenyldithiocarbamate
methyl 3-mercaptobutyrate, stearyldithiocarbamate
decyl 3-mercaptohexanoate, octyldithiocarbamate
triethanolammonium 3-mercaptobutyrate, oleyldithio-carbamate

A most preferred embodiment of this invention is an antiwear-antirust additive for lubricating oils and greases, said additive having the formula:



(II)

wherein R_1 is an aliphatic hydrocarbon radical containing from about 8–100 carbon atoms, R_2 is a divalent aliphatic hydrocarbon radical containing from 2 to about 10 carbon atoms, and R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals containing one to about four carbon atoms. Since the compounds contain both a basic amine functional group and a carboxylic acid they can exist in the form of a zwitterion and are shown in that form in Formula II.

Representative examples of such additives include:

3-mercaptopropionic acid, [2(9-eicosenylamino)ethyl] dithiocarbamate
3-mercapto-2-methylbutyric acid, [6(octylamino)-hexyl] dithiocarbamate
3-mercaptoheptanoic acid, [10(laurylamino)decyl] dithiocarbamate
3-mercapto-2-methylhexanoic acid, [4(1-hexylbutylamino) butyl] dithiocarbamate
3-mercapto-2-butylheptanoic acid, [3(pentacontenylamino) propyl] dithiocarbamate
3-mercaptobutyric acid, [2(hexacontylamino)ethyl] dithiocarbamate
3-mercaptopropionic acid, [3(octacontylamino)propyl] dithiocarbamate
3-mercaptohexanoic acid, [3(C_{100}-polybutenylamino) propyl] dithiocarbamate
3-mercaptobutyric acid, [3(C_{90}-polypropenylamino) propyl] dithiocarbamate
3-mercaptooctanoic acid, [3(dodecenylamino)butyl] dithiocarbamate
3-mercaptopropionic acid, [3(tetracosylamino)propyl] dithiocarbamate
3-mercaptobutyric acid, [6(stearylamino)hexyl] dithiocarbamate
3-mercaptopentanoic acid, [4(palmylamino)butyl] dithiocarbamate
3-mercaptobutyric acid, [3(2-nonacontenylamino)propyl] dithiocarbamate

A preferred class of additives are those of Formula II wherein R_1 contains about 8–22 carbon atoms, R_2 is the trimethylene radical - $(CH_2)_3$ - , R_3 is the methyl radical, and R_4 is hydrogen. Examples of these compounds are:

3-mercaptobutyric acid, [3(oleylamino)propyl] dithiocarbamate

3-mercaptobutyric acid, [3(stearylamino)propyl] dithiocarbamate

3-mercaptobutyric acid, [3(palmylamino)propyl] dithiocarbamate

The additives are readily prepared by reacting an aliphatic hydrocarbylaminohydrocarbylamine with carbon disulfide to form the corresponding hydrocarbylaminohydrocarbyl dithio-carbamic acid and reacting this with an appropriate alpha-unsaturated aliphatic carboxylic acid such as acrylic acid, crotonic acid, α-methyl crotonic acid, α, β-diethyl acrylic acid, β-butyl acrylic acid, α-butyl acrylic acid, and the like (N. Kreutzkamp et al., Arch. Pharm. 304, p. 477–481, July 1971).

The aliphatic hydrocarbylaminohydrocarbylamines can be prepared by reacting an aliphatic hydrocarbyl chloride with an aliphatic diamine. For example, reaction of oleyl chloride with 1,3-propanediamine yields oleylaminopropylamine. Likewise, reaction of lauryl chloride with 1,6-hexanediamine forms laurylaminohexylamine. Similarly, reaction of C_{100}-polybutenyl chloride with ethylenediamine forms C_{100}-polybutenylaminoethyl-amine. The polyolefin chlorides are readily formed by reacting a polyolefin (e.g., polypropylene, polybutene, and the like) with chlorine.

The following example illustrates the manner in which the additives can be prepared.

EXAMPLE 1

To a solution of 175 grams of N-oleyl-1,3-propanediamine and 175 grams of isopropyl alcohol was added a solution of 40 grams of carbon disulfide and 40 grams of isopropyl alcohol over a 1 hour period at 0°–10° C. The unreacted carbon disulfide was distilled off and 50 grams each of crotonic acid, isopropyl alcohol and methanol was added. The mixture was stirred at 0°–10° C. for 2 hours and then allowed to warm to room temperature. The product was diluted with hexane and washed with water, following which volatile material was distilled out under vacuum to yield 184 grams of a low melting solid.

EXAMPLE 2

A portion of the product from Example 1 was diluted with hexane, filtered, water washed, and then the hexane distilled out. The resultant product was diluted with neutral mineral oil to obtain a 67 weight per cent active concentrate. This was diluted with hexane and washed with aqueous ammonia. Powdered solid carbon dioxide was added and stirred into the mixture. The mixture was then water washed, following which hexane was distilled out, leaving a viscous yellow liquid concentrate.

Modification of the above procedure by substitution of different starting hydrocarbylaminohydrocarbylamines and different alpha-unsaturated aliphatic carboxylic acids will lead to the other additives within the scope of this invention.

The additives are useful in lubricating oils and greases including both mineral and synthetic. Synthetic oils include polyolefin oils (e.g., polybutene oil, decene oligomer, and the like), synthetic esters (e.g., dinonyl sebacate, trioctanoic acid ester of trimethylolpropane, and the like), polyglycol oils, and the like. Greases are made from these oils by adding a thickening agent such as sodium, calcium, lithium, or aluminum salts of fatty acids such as stearic acid. The oils and greases are prepared by blending an antiwear and antirust amount of the additive into the oil or grease. A useful concentration is from about 0.1 to 5 weight per cent. The additives may be added in the form of a concentrate such as the mineral oil diluted concentrate described in Example 2.

Other additives may be included in the oil or grease compositions. These include such additives as zinc dialkyl-dithiophosphates, barium phenates, calcium phenates, calcium aryl sulfonates, magnesium aryl sulfonates, overbased calcium aryl sulfonates, barium polybutenyl phosphonates; antioxidants such as 4,4'-methylenebis(2,6-di-tert-butylphenol), α-dimethylamino-2,6-di-tert-butyl-p-cresol; dispersants such as polybutenyl succinimides of ethylenepolyamines, polybutenyl ethylenediamines, viscosity index improvers such as polybutenes, ethylene-propylene copolymers, polylauryl methacrylates, and the like.

Tests have been carried out to demonstrate the antiwear and antirust properties of the additives. The first is known as the "four-ball cam and tappet test." In this test, three steel balls are placed in a triangular manner in a circular retainer containing the test oil. A fourth ball is placed on top of these three to form a triangular pyramid. A 50 Kg load is placed on the top ball and it is rotated at 1,800 r.p.m. for one hour with the oil heated to 110° C. This test has previously been shown to correlate well with the cam and tappet wear of an internal combustion engine. Criteria is the average scar diameter formed on the three bottom balls. A scar diameter of 1 mm or less is considered satisfactory.

The test was carried out on a non-additive neutral oil and on triplicate samples containing 1 weight per cent of the additive of Example 1 — 3-mercaptobutyric acid, [3(oleylamino)-propyl] dithiocarbamate. The results obtained were as follows.

TABLE 1

Additive	Average scar diameter (mm)
None	2.3
Example 1 (1%)	0.92, 0.99, 0.89

The antirust property of the additives was determined using the ASTM D–665 spindle rust test. In this test, spindles are rotated in a mixture of oil and synthetic seawater at 140° F. for 24 hours. The spindles are rated "pass" or "fail." A "pass" rating requires that the spindle be rust-free. This test was carried out using two non-additive mineral oil samples and four samples of the same mineral oil containing 1 weight per cent of the concentrate of Example 2. The results were as follows.

TABLE 2

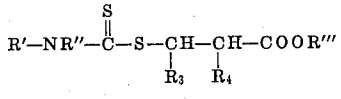
Additive	Results
None	both fail
Example 2 (1%)	all pass

These results demonstrate the excellent antiwear and antirust properties of the present additives.

I claim:

1. A lubricating oil composition comprising major amounts of lubricating oil containing an effective an-

tiwear-antirust amount of an additive, said additive having the formula:

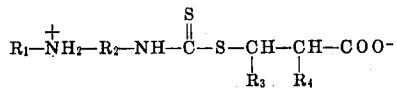


wherein R′ is selected from the group consisting of aliphatic hydrocarbon radicals containing about 8–100 carbon atoms, and hydrocarbylaminohydrocarbyl radicals having the formula:

$$R_1 - NR'''' - R_2 -$$

wherein R_1 is an aliphatic hydrocarbon radical containing about 8–100 carbon atoms, R′′′′ is selected from the group consisting of hydrogen and C_{1-4} alkyls and R_2 is a divalent aliphatic hydrocarbon radical containing about 2–10 carbon atoms, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals containing about 1–4 carbon atoms, R′′ is selected from the group consisting of hydrogen and C_{1-4} alkyl and R′′′ is selected from the group consisting of hydrogen and salt cations, said salt cations selected from the group consisting of alkaline earth metals, ammonium, alkyl amine, alkenyl amine, alkanol amine, zinc, aluminum, nickel, manganese and iron.

2. A lubricating oil composition as defined in claim 1 containing an antiwear-antirust additive wherein said additive has the formula:



wherein R_1 is an aliphatic hydrocarbon radical containing from about 8–100 carbon atoms, R_2 is a divalent aliphatic hydrocarbon radical containing from two to about 10 carbon atoms, and R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals containing one to about four carbon atoms.

3. A lubricating oil composition of claim 2 wherein R_1 contains about 8–22 carbon atoms, R_2 is the trimethylene radical, R_3 is the methyl radical, and R_4 is hydrogen.

4. A lubricating oil composition of claim 3 wherein R_1 is the oleyl radical.

5. A lubricating oil composition of claim 3 wherein R_1 is the stearyl radical.

6. A lubricating oil composition of claim 3 wherein R_1 is the palmyl radical.

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