United States Patent Office 3,112,268 Patented Nov. 26, 1963



3,112,268

# LUBRICATING OIL COMPOSITION

George M. Calhoun, Berkeley, Calif., assignor to Shell Oil Company, New York, N.Y., a corporation of Delaware

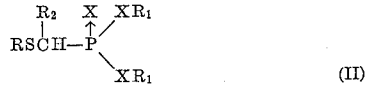
No Drawing. Filed Feb. 15, 1960, Ser. No. 8,498
9 Claims. (Cl. 252—32.7)

This invention relates to improved compounded lubricating oil compositions, particularly crankcase lubricants for internal combustion engines, which are resistant to oxidative deterioration.

Many lubricating oil compositions have been developed for the various uses thereof. In general they are only effective under relatively mild conditions of oxidation, pressure and temperature and are relatively ineffective at high temperatures, extreme pressures and adverse oxidative conditions. Under extreme conditions rapid depletion of the additives used occurs with the ultimate formation of sludge and deposits and the corrosion and wear of the parts being lubricated.

It is an object of this invention to provide a compounded lubricating oil with additives which resist depletion. It is another object of this invention to provide better protection against oxidation of lubricating oils. Still another object is to provide additives which are more resistant to deterioration and which minimize sludge and deposit formation in lubricating oils when subjected to high temperatures and pressures. Other objects will be apparent from the following description of the invention.

It has now been discovered that lubricating oils can be effectively stabilized and extreme pressure and other desirable properties imparted to them by addition of small amounts (0.05–10%, preferably 1–5%, by weight) each of (I) an oil-soluble polythioetherester-ester-ether obtained by reacting (*a*) preferably a full ester of a long chain unsaturated fatty acid and a polyoxyalkylene diol with (*b*) a mercapto acid, mercapto alcohol, mercapto ether or mercapto ester so that the end product contains at least one thioether radical in the molecule and (II) an oil-soluble 2-thia-alkyl phosphono-containing compound having the general formula



(II)

wherein R is an oil-soluble hydrocarbyl group such as alkyl, aryl, aralkyl, alkaryl or cycloalkyl radical having at least 6 carbon atoms and preferably a straight-chain alkyl radical having from 10 to 18 carbon atoms, the $R_1$'s are the same or different groups selected from hydrogen, hydrocarbyl or cationic groups, such as metallic or nonmetallic cationic groups, e.g., mono or polyvalent metal or amine, preferably an alkylamine $R_2$ is hydrogen or a $C_{1-4}$ alkyl radical and the X's are independently selected chalcogen atoms having an atomic number of from 8 to 16, i.e., oxygen or sulfur.

The oil-soluble additive (I) is obtained by reacting (*a*) an ester of a long chain unsaturated fatty acid, RCOOH, and a polyoxyalkylene diol or its thio derivative having the formula.

$$HO-\left(R''-X\right)_x\left(R'-O\right)_y-H \qquad (III)$$

where R′ and R″ are the same or different alkyl radicals of from 2 to 8, preferably 2 to 3, carbon atoms, X is oxygen or sulfur, as it is in Formula II, and *x* and *y* are integers of at least 1, preferably 1 to 6 with (*b*) a mercapto compound, $HS(CH_2)_nZ$, such as a mercapto acid, alcohol, ether or ester so that the end product has at least 1 and preferably 2 thioether radicals, $—S(CH_2)_nZ$, wherein Z is —OR‴ or —COOR‴ and the R‴ is hydrogen



or a $C_{1-4}$ alkyl radical and *n* is an integer of from 1 to 4, preferably 1. The maximum number of

$$-S\left(CH_2\right)_n-Z$$

units in the final compound depends on the degree of unsaturation of the intermediate ether-ester and the extent to which they have been reacted with the mercapto compound. The unsaturated fatty acid ester of the polyoxyalkylene glycol may be represented by the corresponding formula

$$RCOO-\left(R''-X\right)_x\left(R''-O\right)_y-OCR \qquad (IV)$$

and the thioether thereof by the formula

$$X'-\left(CH_2\right)_n-S-R-COO-\left(R''-X'\right)_x\left(R'-O\right)_y-CO\cdot R-S-(CH_2)_nZ \qquad (V)$$

The intermediate ether-esters are prepared by esterifying a long chain unsaturated fatty acid such as oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid and the like with a polyoxyalkylene diol or the thio derivatives thereof, such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, 2,2′-thiodiethanol, 3,3′-thiodipropanol, and the like. Esters of these materials include diethylene glycol dioleate, triethylene glycol dioleate, dipropylene glycol dioleate, diethylene glycol linoleate, tetraethylene glycol ricinoleate, dibutylene glycol oleate, 2,2′-thiodiethanol dioleate, 2,2′-thiodiethanol diricinoleate, 2,2′-thiodiethanol linoleate and the like.

Compounds of the present invention are prepared by reacting the ether-ester with a mercapto compound such as mercapto aliphatic carboxylic acids, e.g., mercaptoacetic acid, mercaptopropionic acid, mercaptobutyric acid, or mercapto-alkanols such as 2-mercaptoethanol, 2- and 3-mercaptopropanol, 2-, 3- and 4-mercaptobutanol or ethers of said mercaptoalcohols such as methyl or octyl 2-mercaptoethyl ether or mercapto esters, e.g., ethyl mercaptoacetate or ethyl mercaptobutyrate, and mixtures thereof.

The additives can be prepared by the methods described by Koenig et al. JACS, 79, 362 (1957), or Fitzgerald, Jr. Org. Chem., 22, 197 (1957), preferably at low temperatures, from room temperature to about 50° C., in the presence of a free radical catalyst such as azo or peroxide catalysts or ultraviolet light and a non-reactive solvent such as benzene, toluene, xylene, or the like. Suitable initiators include various free radical-yielding, aliphatic (acyclic and alicyclic) and heterocyclic peroxides, such as diethyl peroxide, tertiary butyl hydroperoxide, dibenzoyl peroxide, ditertbutyl peroxide, dimethylthienyl peroxide, dicyclohexyl peroxide, dilauroyl peroxide and urea peroxide. These are mentioned by way of non-limiting examples of suitable organic peroxides. Other initiating substances include redox systems, such as a mixture of sodium bisulfite and persulfate, ammonium persulfate and alkali metal perborates.

The following examples illustrate the preparation of suitable additives for use in accordance with the present invention.

## EXAMPLE I

About 600 grams of diethylene glycol dioleate and 223.5 grams of mercaptoacetic acid were mixed in a flask at 20–25° C. About 240 drops (30 drops at a time) of t-butyl hydroperoxide were added over a period of 2 hours and the temperature was kept at about 37° C. The reaction mixture was diluted with 2 volumes of diethyl ether, washed with 12 liters of water to pH 4, dried over $Na_2SO_4$, filtered and the solvent stripped at 155° C. and 2 mm. pressure. The final product was a

mixture of the 9- and 10-carboxymethylmercaptostearate diesters of diethylene glycol.

## EXAMPLE II

About 600 grams of triethylene glycol dioleate and 223.5 grams of mercaptoacetic acid were mixed in a flask at 20–25° C. About 240 drops (30 drops at a time) of t-butyl hydroperoxide were added over a period of 2 hours and the temperature was kept at about 37° C. The reaction mixture was diluted with 2 volumes of diethyl ether, washed with 12 liters of water to pH 4, dried over $Na_2SO_4$, filtered and the solvent stripped at 155° C. and 2 mm. pressure. The final product was a mixture of the 9- and 10-carboxymethylmercaptostearate diester of triethylene glycol.

## EXAMPLE III

About 600 grams of diethylene glycol ricinoleate and 223.5 grams of mercaptoacetic acid were mixed in a flask at 20–25° C. About 240 drops (30 drops at a time) of t-butyl hydroperoxide were added over a period of 2 hours and the temperature was kept at about 37° C. The reaction mixture was diluted with 2 volumes of diethyl ether, washed with 12 liters of water to pH 4, dried over $Na_2SO_4$, filtered and the solvent stripped at 155° C. and 2 mm. pressure. The final product was a mixture of the 9- and 10-carboxymethylmercapto-12-hydroxystearate diester of diethylene glycol.

## EXAMPLE IV

About 600 grams of diethylene glycol dioleate and 223.5 grams of mercaptoethanol were mixed in a flask at 20–25° C. About 240 drops (30 drops at a time) of t-butyl hydroperoxide were added over a period of 2 hours and the temperature was kept at about 37° C. The reaction mixture was diluted with 2 volumes of diethyl ether, washed with 12 liters of water to pH 4, dried over $Na_2SO_4$, filtered and the solvent stripped at 155° C. and 12 mm. pressure. The final product was a mixture of diethylene glycol di(9- and10-[2-hydroxyethylmercapto]stearate).

## EXAMPLE V

About 600 grams of 2,2'-thiodiethanol dioleate and 223.5 grams of mercaptoacetic acid were mixed in a flask at 20–25° C. About 240 drops (30 drops at a time) of t-butyl hydroperoxide were added over a period of 2 hours and the temperature was kept at about 37° C. The reaction mixture was diluted with 2 volumes of diethyl ether, washed with 12 liters of water to pH 4, dried over $Na_2SO_4$, filtered and the solvent stripped at 155° C. and 2 mm. pressure. The final product was a mixture of 2,2'-thiodiethanol di(9- and 10-carboxymethylmercaptostearate).

The oil-soluble-2-thiaalkylphosphono compounds represented by Formula II are prepared by reacting a mercaptan or mercaptide having at least 6 carbon atoms with a halomethylphosphono compound such as chloromethylphosphonic acid or a chloromethylphosphonate or their thio derivatives in a suitable solvent, such as an aqueous alcoholic solution, at reflux temperature and under inert conditions until the reaction is completed, which may require up to about 5 days in some cases. The mercaptans include acylic aliphatic mercaptans, such as hexyl, octyl, decyl, dodecyl, octadecyl mercaptans; cycloalkyl mercaptans, such as cyclohexyl mercaptan; aralkyl mercaptans such as phenyldecyl mercaptan, benzyl mercaptan; and aryl-mercaptans such as phenyl mercaptan. Instead of the mercaptans, the mercaptides can be used such as the alkali metal (Na or K) mercaptides of the above compounds. Suitable halomethylphosphono compounds include chloromethylphosphonic acid, mono or dihydrocarbyl chloromethylphosphonates, e.g., mono or dibutyl chloromethylphosphonate, mono or di-2-ethylhexyl chloromethylphosphonate, mono or dicyclohexyl chloromethylphosphonate, mono or dibenzyl chloromethylphosphonate, dibutyl dithiochloromethylphosphonate, diphenyl chloromethyl dithiophosphonate, dibutyl chloromethyltrithiophosphonate, alkali metal salts such as Na and K salts of chloromethylphosphonic acid, Na and K salts of monobutyl chloromethylphosphonic acid, Na and K salt of monodecyl chloromethylphosphonic acid and the like.



A preferred method of making the 2-thiaalkylphosphonates is to react a suitable mercapto compound, such as an alkali metal (Na or K) $C_{10-18}$ alkyl mercaptide with an alkali metal (Na and K) salt of chloromethylphosphonic acid in an alcoholic solution under reflux conditions and under an inert atmosphere to form the alkali metal salt of an alkylmercaptomethylphosphonic acid. The salt is then treated with a strong acid such as hydrochloric acid to spring the free alkylmercaptomethylphosphonic acid, which can be converted into desired partial or full esters or polyvalent metal salts or amine salts for use as oil, fuel and grease additives as well as other uses.

The following examples illustrate the preparation of the 2-thiaalkylphosphono additives for use in accordance with the present invention.

### *Example A*

Stoichiometric amounts of the potassium salt of decyl mercaptan and monochloromethylphosphonic acid were dispersed in an aqueous solution of ethyl alcohol and the mixture was refluxed at 78° C. under a nitrogen atmosphere for about 1 day. The reaction mixture was then treated with strong hydrochloric acid and the free decylmercaptamethylphosphonic acid was recovered by extraction with ether. The final product decylmercaptomethylphosphonic acid analyzed as follows.

| | Percent Ce | Percent H | Percent S | Percent P | Equiv. wt. 1st hydrogen | Equiv. wt. both hydrogens |
|---|---|---|---|---|---|---|
| Found | 49.1 | 9.4 | 12.0 | 11.2 | 261 | 132 |
| Expected | 49.2 | 9.4 | 11.94 | 11.54 | 268.3 | 134.1 |

### *Example B*

The procedure of Example A was followed except that the potassium salt of phenylmercaptan was used instead of the potassium salt of decylmercaptan and the final product was phenylmercaptomethylphosphonic acid.

### *Example C*

The butyl ester of the decylmercaptomethylphonic acid of Example A was prepared by treating dibutyl monochloromethylphosphonate wtih the K salt of decylmercaptan in an alcoholic solution at about 60° and extracting the ester with ether.

### *Example D*

Di-2-ethylhexylamine salt of decylmercaptomethylphosphonic acid (2-thiadodecylphosphonic acid) was prepared by mixing the acid product of Example A with di-2-ethylhexylamine in an amount sufficient to completely neutralize both acid groups, at room temperature to form the amine salt.

### *Example E*

Tert-octadecylamine salt of decylmercaptomethylphosphonic acid was prepared by mixing the acid product of Example A with tert-octylamine in an amount sufficient to completely neutralize both acid groups, at room temperature. The tert-octylamine is prepared by the method described in Ind. Eng. Chem., Nov. 1959.

The following additional compounds were prepared: Octyl-mercaptomethylphosphonic acid, dodecylmercaptomethylphosphonic acid, cyclohexylmercaptomethylphosphonic acid, benzylmercaptomethylphosphonic acid, phenylmercaptomethylphosphonic acid, monobutyl and dodecyl-dibutyl mercaptomethylphosphonate, phenyldecylmercaptomethyl acid phosphonate, dithiobutyl dodecylmercaptomethylphosphonate, dibutyl phenylmercaptomethylphosphonate, dithiooctyl cyclohexylmercaptomethylthiophosphonate, dioctylamine dodecylmercaptomethylphosphonate, diotadecylamine phenylmercaptomethyl-

phosphonate, tert-octadecylamine dodecylmercaptomethylphosphonate and mixtures thereof.

Lubricating oils useful for the preparation of compositions of this invention can be one or more of a variety of synthetic oils or natural hydrocarbon oils having a viscosity range of from 50 SUS at 100° F. to 250 SUS at 210° F. (SAE viscosity number ranging from SAE 10W to SAE 90). The natural hydrocarbon oils can be obtained from paraffinic, naphthenic, asphaltic or mixed base crudes, and/or mixtures thereof refined as by extraction, acid treatment, and clay treatment. Synthetic oils include polymerized olefins, alkylated aromatics, isomerized waxes, copolymers of alkylene glycols and alkylene oxide (Ucon fluids) which are described in U.S. Patents 2,425,755, 2,425,845 and 2,774,733 such as Ucon 50HB170, Ucon 50HB660 or Ucon LB550X and which are copolymers of ethylene and 1,2-propylene oxides, the mono- and diols, as well as their ether derivatives; organic esters of aliphatic dibasic acids such as di-2-ethylhexyl sebacate or di-2-ethylhexyl adipate and the like. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or synthetic oils as mentioned or silicone polymers and the like.

Typical useful oils include petroleum base motor oils of the (A) paraffinic type and (B) naphthenic type having representative properties as follows:

| | (A) (SAE 10W) | (B) (SAE 30) |
|---|---|---|
| Pour point, ° F | −10 | −5 |
| Flash, ° F | 390 | 415 |
| Viscosity, SUS at 210° F | 44 | 58 |
| Viscosity index | 90 | 60 |

Other suitable oils are the 1010 and 1065 grade gas turbine lube oils represented by the following:

| Grade | 1010 | 1065 |
|---|---|---|
| Flash, COC, ° F | 300 | 465 |
| Pour, ° F | −10 | 0 |
| Viscosity, SUS at 100° F | 59.4 | 530 |
| Neutral number | 0.02 | 0.01 |
| Ash | None | None |

The following compositions composed essentially of the materials indicated are illustrative of the invention, wherein "Example I" and the like refer to the product of the indicated example, the percentages being by weight.

| | Percent |
|---|---|
| Composition A: | |
| Example I | 4 |
| Example A | 1 |
| Mineral oil (1010) | Balance |
| Composition B: | |
| Example I | 4 |
| Example C | 1.42 |
| Mineral oil (1010) | Balance |
| Composition C: | |
| Example I | 4 |
| Dibutyl dodecyl 2-thiamethylphosphonate | 1.21 |
| Mineral oil (1010) | Balance |
| Composition D: | |
| Example II | 3 |
| Example C | 1.5 |
| Mineral oil (SAE 90) | Balance |
| Composition E: | |
| Example III | 5 |
| Example D | 2 |
| Mineral oil (SAE 30) | Balance |
| Composition F: | |
| Example I | 2 |
| Example C | 1 |
| Di-2-ethylhexyl sebacate | Balance |

Compositions of this invention were tested for their ability to resist additive depletion by heating the test oil at 150° C. in the presence of air and thereafter potentiometrically titrating a sample of the oil to determine the amount of depletion which had occurred. With compositions A to E containing the additive combination only 10–20% of the total additives were depleted. On the other hand, a 1010 mineral oil containing as much as 4% of the additive of Example A or a 1010 mineral oil containing 4% of additive of Example C showed depletion of 80–90% and 1010 mineral oil containing 4% of additive of Example I showed additive depletion of 40–50%.

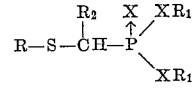


Lubricants of the present invention (Compositions A–F) also possess excellent extreme pressure properties as evaluated on the Spur-Gear Machine (Lubricating Engineering, January-February 1956) carrying loads of 15,000 lbs./in. at 3200 r.p.m. and 100° C. oil temperature, whereas the base oil (1010 mineral oil) carries a load of 600 lbs./in.

The additive combinations of this invention are useful also for providing superior load-carrying properties for lubricating oils which contain minor amounts of other agents, such as silicone anti-forming agents, alkylphenol and bisphenol anti-oxidants, polyacrylate ester viscosity-index improvers, long chain acids such as lauric and oleic acids as oiliness agents and the like.

I claim as my invention:

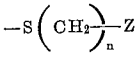
1. A lubricating oil containing from about 0.05% to about 10% each of (1) an oil-soluble dicarboxy $C_{1-4}$ alkyl mercapto substituted diester of an unsaturated fatty acid having at least 18 carbon atoms and an alkylene glycol and a diol selected from the group consisting of polyoxyalkylene diol and its sulfur analogue the alkylene portion containing 2 to 4 carbon atoms and (2) an oil-soluble alkylmercaptomethylphosphono compound having the general formula



wherein R is an oil-soluble alkyl radical having from 6 to 18 carbon atoms, the $R_1$'s are selected independently from the group consisting of hydrogen, alkyl radical having from 4 to 18 carbon atoms and an aliphatic amine having from 8 to 18 carbon atoms, $R_2$ is selected from the group consisting of hydrogen and $C_{1-4}$ alkyl radical, and X is a chalcogen having an atomic number from 8 to 16.

2. The composition of claim 1 where the additive (1) is dicarboxy $C_{1-4}$ alkyl mercapto substituted diester of a long-chain unsaturated fatty acid having at least 18 carbon atoms and diethylene glycol and wherein additive (2) R is a $C_{10-18}$ alkyl radical, one of the $R_1$'s is hydrogen and the other $R_1$ is a $C_{4-18}$ alkyl radical and X is oxygen.

3. The composition of claim 2 where the oil is a mineral lubricating oil, the mercapto-containing portion of the ester is



where Z is oxygen containing radical selected from the group consisting of —OR''' and —COOR''' where R''' is hydrogen and a $C_{1-4}$ alkyl radical and $n$ is an integer of from 1 to 4 and (2) $C_{10-18}$ alkylmercaptomethylphosphonic acid.

4. A mineral lubricating oil containing from about 0.05% to about 10% each of (1) an oil-soluble dicarboxy $C_{1-4}$ alkylmercapto-substituted stearate diester of polyethylene glycol and (2) an ester of $C_{10-18}$ alkyl mercaptomethylphosphonic acid the ester being selected from the group consisting of mono and diester of a $C_{4-18}$ alkanol and $C_{10-18}$ alkyl mercapto methyl phosphonic acid.

5. A mineral lubricating oil containing from about 0.5% to about 10% each of (1) an oil-soluble di(carboxy $C_{1-4}$ alkylmercapto)2,2'-thiodiethanol dioleate substituted ester of oleic acid and polyoxyethylene glycol and (2) an ester of $C_{10-18}$ alkylmercaptomethylphosphonic acid the ester being selected from the group consisting of mono

and diester of a $C_{4-18}$ alkanol and $C_{10-18}$ alkyl mercapto methyl phosphonic acid.

6. A mineral lubricating oil containing from about 1% to about 5% each of di(carboxymethylmercaptostearate) diester of diethylene glycol and monobutyl decylmercaptomethylphosphonate.

7. A mineral lubricating oil containing from about 1% to about 5% each of di(carboxymethylmercapto)2,2'-thiodiethanol dioleate and monobutyl decylmercaptomethylphosphonate.

8. A mineral lubricating oil containing from about 1% to about 5% each of a mixture of 9- and 10-carboxymethylmercaptostearate diester of diethylene glycol and monobutyl decylmercaptomethylphosphonate.

9. A mineral lubricating oil containing from about 1% to about 5% and 2,2'-thiodiethanol di(9- and 10-carboxymethylmercaptostearate) and monobutyl decylmercaptomethylphosphonate.



**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,329,707 | Farrington et al. | Sept. 21, 1943 |
| 2,535,174 | Tawney | Dec. 26, 1950 |
| 2,603,654 | Kosmin | July 15, 1952 |
| 2,724,718 | Stiles et al. | Nov. 22, 1955 |
| 2,971,019 | Ladd et al. | Feb. 7, 1961 |
| 2,994,662 | Calhoun et al. | Aug. 1, 1961 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 751,755 | Great Britain | July 4, 1956 |
| 763,543 | Great Britain | Dec. 12, 1956 |
| 804,141 | Great Britain | Nov. 12, 1958 |