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HYDROCARBON OIL LUBRICANT CONTAINING DI-TERTIARY-ALKYL SULFIDES

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8 Claims. (Cl. 252—45)

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The present invention pertains to sulfur derivatives of hydrocarbons as additives for hydrocarbon lubricants.

The compounds of the invention are, for the most part, sulfur derivatives of aliphatic hydrocarbons and are dialkyl sulfides containing two or more sulfur atoms interconnecting the respective alkyl radicals, each of which is a tertiary alkyl radical containing from 8 to 25 carbon atoms. These compounds are made by condensing with hydrogen sulfide a branched chain olefin providing the desired tertiary carbon configuration in the resulting mercaptan, and oxidizing the mercaptan to form the corresponding sulfide or mixture of sulfides having at least two sulfur atoms interconnecting the two alkyl radicals of the compound.

The resulting compounds, when added to petroleum lubricants, improve the ability of the lubricants to withstand high pressures and to remain stable under high temperatures and oxidizing conditions. They also serve as valuable additives when combined with cutting oils. The mercaptans formed as intermediates also have these lubricant improving properties, and the use of the mercaptans as well as the sulfides in this connection falls within the scope of the invention.

In the practice of the invention, the intermediate mercaptans may be derived from any source, such as, by the process of the prior applications of John F. Olin and John L. Eaton jointly, Serial No. 472,946, filed January 20, 1943, and which has matured into Patent No. 2,434,510, granted January 13, 1948.

As an illustration of one preferred product of the invention and the process of manufacture thereof, the invention will be described specifically with reference to the production of di-tertiary dodecyl sulfides having at least two sulfur atoms, and usually from 2 to 4 sulfur atoms, linking the respective tertiary dodecyl radicals. I wish it to be understood that this form of description is adopted solely for the purpose of illustration without intention to limit the invention, as other compounds of the invention containing between 8 and 25 carbon atoms may be formed in a manner similar to that described herein for manufacture of tertiary dodecyl sulfides. For example, the invention includes tertiary decyl compounds formed from diamylenes, tertiary hexadecyl compounds formed from tetra-butylenes, tertiary pentadecyl mercaptans formed from triamylenes, and similar compounds containing up to 25 carbon atoms in the respective alkyl radicals. The invention includes not only compounds

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formed from polymers of individual olefins, but also compounds formed from co-polymerization of different olefins. Thus, for example, tertiary tridecyl mercaptan may be formed by polymerization of two molecules of amylene with a single molecule of propylene, followed by condensation of the resulting tri-decylene with hydrogen sulfide, and this mercaptan may then be oxidized to form a di-tertiary tri-decyl polysulfide.

After formation of the tertiary dodecyl mercaptan, this mercaptan is oxidized to produce the desired di-tertiary dodecyl polysulfide. (By this term I mean to include compounds containing two sulfur atoms linking the respective tertiary alkyl radicals, as well as the more highly sulfurized polysulfides.)

The process of oxidation is preferably accomplished in accordance with the process of my prior patents, 2,237,625 and 2,237,627, both patented April 8, 1941. Thus, by mixing the mercaptan with sulfur and adding a small amount of a basic catalyst, the oxidation (sulfurization) reaction may be made to proceed with considerable rapidity, and a mixture of di-tertiary dodecyl di-, tri- and higher- sulfides may be formed. These various sulfides may be separated from each other or they may be used in the form of a mixture as an additive to a petroleum oil to be used as a lubricant. In case a product of higher degree of sulfurization than that obtained by the process described above is desired, the product of initial oxidation (sulfurization) may be subjected to further oxidation as taught in my prior Patent 2,237,627.

The products of the invention may be added to petroleum oils intended for use as lubricants and as cutting oils. When a lubricant product is prepared by addition of a minor part of a sulfide of the invention to a major part of lubricating oil, the resulting lubricant is much improved in its capacity to withstand high pressures, temperatures and oxidizing conditions, as compared with the corresponding hydrocarbon oil in an untreated condition. In this connection, the sulfur derivative may be added in varying proportions form a mere trace to as much as 10%. As petroleum lubricating oil derivatives, there may be used not only the dialkyl polysulfides of the invention, but also the corresponding mercaptans formed as intermediates in the practice of the present invention.

Example I

404 grams (2 moles) of tertiary dodecyl mercaptans, 146 grams monobutylamine and 1 gram of copper acetate were placed in a one liter flask

to which was attached a reflux condenser. Passing below the surface of the liquid was a tube bearing a porous gas disperser. A slow stream of oxygen was then led into the mixture. A mild exothermic reaction took place with absorption of the oxygen. After several hours the solution turned dark blue and no further gas was absorbed. The mixture was then washed with several portions of water, treated with diatomaceous earth and filtered to yield a clear yellow colored oil which contained 14.91% sulfur.

Example II

641 grams of a crude reaction mixture resulting from sulfhydration of tri-isobutylene, and containing 94.7% tertiary dodecyl mercaptans were placed, together with 57.6 grams of sulfur and 1 gram of tributylamine, in a flask fitted with a stirrer and reflux condenser. The mixture was now heated at 105° C. for a period of six hours during which time considerable evolution of hydrogen sulfide occurred. The batch was finished by heating for one hour at 160° C., after which it was cooled and treated with 230 grams of $Na_2S \cdot 9H_2O$ with stirring at 80° C. This treatment removed uncombined sulfur. It was then thoroughly washed with water and dried by aeration. The yield was 600 grams of a light yellow colored oil containing 15.9% sulfur.

Example III

404 grams of tertiary dodecyl mercaptans were dissolved in an equal quantity of benzene, and the mixture was placed in a three-necked flask, equipped with a thermometer, reflux condenser and dropping funnel. The mixture was warmed to 80° C. and 103 grams of sulfur dichloride were introduced over a period of ½ hour, during which time hydrogen chloride was disengaged. It was then refluxed for an additional two hours, poured into an excess of 5% sodium hydroxide solution and the benzene was distilled out. The oil layer was dried with calcium chloride. It was a clear yellow-orange colored liquid possessing a specific gravity at 20° C. of 0.948. It contained 23% sulfur compared to a theoretical of 22.2% for dodecyl trisulfide.

Example IV

Tertiary dodecyl tetrasulfide was made in a manner similar to that employed for the trisulfide except that sulfur monochloride was used in place of the sulfur dichloride. The tetrasulfide was obtained as a deep orange colored liquid, which possessed a specific gravity at 20° C. of 0.984. The sulfur content was 24.9% compared to a theoretical of 26.4% for dodecyl tetrasulfide.

While the invention has been described above with reference to manufacture of mercaptans and sulfides from relatively pure olefins resulting from polymerization of lower olefins, it should be understood that it is not necessary to use such a relatively pure source of olefinic material. Thus, mixtures of various tertiary olefins containing between 8 and 25 carbon atoms may be used in practice of the invention, and the respective alkyl groups attached to a given sulfur bridge are not necessarily identical. Thus, for example, mixed polysulfides containing dodecyl and hexadecyl radicals may be made and used in practice of the invention, and an advantage of the invention consists in the fact that it may be practiced in the use of olefinic mixtures, without the necessity of the very careful fractionation which would be necessary as a preliminary step to manufacture of relatively pure compounds.

While the polysulfides and the mercaptans used as petroleum additives in practice of the invention will ordinarily consist of, or at least predominate in, open chain aliphatic compounds, they may consist of, or include, cycloaliphatic compounds, within the broad spirit of the invention. It is well known that, when olefins are polymerized either thermatically or catalytically, cyclo-olefins may be produced as the principal constituent or a minor constituent of the reaction mixture, and the invention comprehends products obtained by sulfhydration of such alicyclic olefins and subsequent oxidation of the resulting mercaptans, whether such alicyclic olefins are merely a part of a mixture of polymerized olefins including or predominating in open chain polymers, or whether such alicyclic olefins are used as a relatively pure fraction. The tertiary open chain products are, however, the most important products of the invention.

Example V

A qualitative test as to the effectiveness of hypoid lubricants is afforded through the corrosiveness of solutions of the additive in oil at 100° C. and at 149° C. for a period of one hour. (General Motors Standards, volume II, pp. D–5 and D–6, July 1939.) A polished copper strip immersed in the oil solution should give a color not darker than a peacock blue at 100° C., but at 149° C. it should give a color which is dark brown to black. This indicates that an additive is stable under mild conditions but is active under more rigorous conditions. Samples of tertiary dodecyl di-, tri- and tetra-sulfides gave unsatisfactory results under this test.

The tertiary dodecyl compounds of the present invention were also evaluated as extreme pressure lubricants by use of the Timken lubricant testing machine (Journal Society Automotive Engineers, volume 28, page 53, 1931) at the standard speed of 800 R. P. M., rubbing speed of 400 ft. per minute. The oil solutions were prepared in a Pennsylvania type lubricating oil of S. A. E. 40 viscosity. The solutions contained concentrations of the respective additives which, in every case, provided 1.5% of sulfur, based upon the amount of lubricant. The following results were obtained:

Test No.	Additive	Concentration	O. K. Load, lbs./sq. in.	Score Load, lbs./sq. in.
		Per cent		
1	None		5,000	6,000
2	t-dodecyl mercaptans	9.47	15,000	20,000
3	t-dodecyl disulfides	9.4	20,000	25,000
4	t-dodecyl trisulfides	6.8	20,000	25,000
5	t-dodecyl tetrasulfides	5.8	15,000	20,000

Abrasion losses, tested by running the Timken machine under a load of 12,000 lbs. per square inch for six hours, were between 3.8 milligrams and 6.2 milligrams. Most commercial lubricants show an abrasion of 1.5–15 milligrams.

Various other modifications are possible within the scope of the invention, and I do not therefore wish to be limited except by the scope of the following claims.

I claim:

1. An improved lubricant comprising a major portion of a hydrocarbon oil and up to 10% of an added organic sulfur compound comprising a dialkyl sulfide having tertiary alkyl radicals of

from 8 to 25 carbon atoms and having from 2 to 4 sulfur atoms linking the respective tertiary alkyl radicals.

2. An improved lubricant comprising a major proportion of a hydrocarbon oil and a minor but sufficient proportion to stabilize the hydrocarbon oil against oxidation of an added organic sulfur compound comprising a dialkyl sulfide having tertiary alkyl radicals of from 8 to 25 carbon atoms and having from 2 to 4 sulfur atoms linking the respective tertiary alkyl radicals.

3. An improved lubricant comprising a major portion of a hydrocarbon oil and up to 10% of an added organic sulfur compound comprising a di-tertiary dodecyl sulfide having from 2 to 4 sulfur atoms linking the respective tertiary dodecyl radicals.

4. An improved lubricant comprising a major proportion of a hydrocarbon oil and a minor but sufficient proportion to stabilize the hydrocarbon oil against oxidation of an added organic sulfur compound comprising a di-tertiary dodecyl sulfide having from 2 to 4 sulfur atoms linking the respective tertiary dodecyl radicals.

5. An improved lubricant comprising a major portion of a hydrocarbon oil and up to 10% of an added organic sulfur compound comprising a dialkyl disulfide having tertiary alkyl radicals of from 8 to 25 carbon atoms.

6. An improved lubricant comprising a major portion of a hydrocarbon oil and up to 10% of an added organic sulfur compound comprising di-tertiary dodecyl disulfide.

7. An improved lubricant comprising a major portion of a hydrocarbon oil and up to 10% of an added organic sulfur compound comprising an organic sulfide consisting of two organic radicals derived from polymerized olefin and containing from 8 to 25 carbon atoms interconnected by from 2 to 4 sulfur atoms linking said radicals.

8. An improved lubricant comprising a major proportion of a hydrocarbon oil and a minor but sufficient proportion to stabilize the hydrocarbon oil against oxidation, of an added organic sulfide compound comprising di-tertiary dodecyl disulfide.

JOHN F. OLIN.

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