

- [54] **POLYSULFURIZED OLEFINS**
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Related U.S. Application Data

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[51] Int. Cl.....C07c 161/00
[58] Field of Search.....260/125, 139

References Cited

UNITED STATES PATENTS

- 2,249,312 /1941 Kimball260/139
2,467,713 /1949 Watkins.....252/139 X

2,708,199 /1955 Eby.....260/139 X

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[57] **ABSTRACT**

Sulfurized olefins are produced by (1) reacting sulfur monochloride with a stoichiometric excess of a low-carbon atom olefin, (2) treating the resulting product with an alkali metal sulfide in the presence of free sulfur in an alcohol-water solvent, and (3) reacting that product with an inorganic base. This reaction sequence produces novel stable oil-soluble organic sulfides having extreme pressure properties and low corrosiveness to metal. Lubricating oil compositions containing an effective amount of these additives evidence good load carrying capability.

10 Claims, No Drawings

POLYSULFURIZED OLEFINS

CROSS-REFERENCE TO RELATED INVENTIONS

This application is a division of copending application Ser. No. 620,621, filed Mar. 6, 1967, now U.S. Pat. No. 3,471,404.

FIELD OF THE INVENTION

This invention relates to sulfurized olefins and in particular to polysulfurized olefins used in lubricating oil compositions and to a method for preparing the same.

DESCRIPTION OF PRIOR ART

Organic sulfur compounds have been known as additives for lubricating oils. These compounds provide extreme pressure properties to lubricants especially under high speed shock conditions. Unfortunately, the presence of sulfur in lubricating oils causes considerable corrosion of metals, particularly copper. Since lubricating oils often operate at relatively high temperatures, thermally unstable sulfur compounds may break down resulting in loss of the extreme pressure property and in increased metal corrosion. In U. S. Pat. No. 2,708,199, there is disclosed a method of producing organic polysulfides from olefins having from six to 30 carbon atoms resulting in polymers of the olefin containing two to three sulfur atoms per unsaturated bond of the olefin. However, without proper control of the reaction conditions, the resulting compound may be highly corrosive and unstable. Moreover, if olefins of less than six carbon atoms were used in this process, oil insoluble products would be obtained.

SUMMARY OF THE INVENTION

It has now been unexpectedly discovered that novel stable non-corrosive organosulfur compounds which are substantially monomeric may be prepared by the steps of (1) reacting a sulfur chloride with an excess of an olefin, (2) reacting the resulting adduct with an alkali metal sulfide and free sulfur in a mole ratio of no less than 2:1 and (3) treating the product of step (2) with an inorganic base.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The olefin reactant used in this invention may contain from about two to about five carbon atoms. The preferred number of the carbon atoms of the olefin ranges from three to about five. Such olefins as butylene, isobutylene or amylene and isoamylene may be used; in particular, the branched-chain olefins are the most preferred in accordance with this invention. It has been herein discovered that isobutylene has unexpectedly greater reactivity to sulfur chloride than other olefins and yields highly stable reaction products.

In the first step, sulfur monochloride is reacted with from 1 to 2 moles, and preferably from 1.25 to 1.8 moles, of the olefin per mole of the sulfur monochloride. The reaction is carried out by mixing the two reactants at a temperature from 20° C. to about 80° C. and preferably 30° to 50° C. The olefin is introduced into the liquid sulfur monochloride subsurface, at a rate commensurate with the absorption rate of the olefin into the sulfur monochloride. This reaction may take from a period of from 1 to 10 hours, although it is preferred that the reaction time be carried out as rapidly as possible.

The second step in the process of this invention requires reacting the adduct of the first step with an alkali metal sulfide and free sulfur. In this reaction, the adduct is combined with a mixture of the alkali metal sulfide, preferably sodium sulfide, and sulfur. The mixture consists of up to about 2.2 moles of the metal sulfide per gram-atom of sulfur and preferably the ratio is 1.8 to 2.2. The mole ratio of alkali metal sulfide to adduct is about 0.8 to about 1.2 moles of metal sulfide per mole of adduct. These ratios are both considered significant in the practice of this invention. They have been found to contribute to the oil solubility and thermal stability of the final product. This reaction, furthermore, is carried out in the presence of an alcohol or an alcohol-water solvent under reflux conditions. The alcohol may be present in a concentration in the water of from 5 percent to 25 percent by weight. Water-soluble alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, and the like, may be used. The reflux time ranges from 3 to 6 hours.

The third step in the process of this invention is the reaction between the polysulfurized olefin, which contains from about 1 to about 3 percent of chlorine, with an inorganic base in a water solution. Alkali metal hydroxide may be used, particularly sodium hydroxide, at a concentration of about 5 to about 20 percent and preferably about 8 to 12 percent, by weight in water. The reaction must be continued until the chlorine content is below 0.5 percent. The concentration of the alkali metal hydroxide in water also appears to be of an important nature in the preparation of the desirable product, and therefore the preferred range represents an effective concentration level. Higher concentrations may degrade the product severely and lead to reaction products which could not be separated from the reaction mass easily. The alkali metal hydroxide treatment of the polysulfurized olefin is performed under reflux conditions for from 1 to 24 hours, although no more than 8 hours are usually sufficient. Other inorganic bases which may be used include alkali metal carbonates and ammonia. However, the alkali metal hydroxides, and particularly sodium hydroxide, produce the most desirable product as evidenced by the low degree of corrosiveness to copper metal.

The exact structure of the product is not known. It may consist of monomers containing sulfur or monomers bridged in a cyclic structure by the sulfur. It is believed that about 75 percent or more of the product is made up of monomeric sulfides and the cyclic derivatives thereof. An important feature of these oil-soluble polysulfurized olefins is that the products of this invention contain from about 40 to about 60 percent, preferably 46 to 50 percent, sulfur in stabilized form, and less than 0.5 percent chlorine. Although the broadly described process may yield products having utility in lubricating compositions, the products produced by adhering to the express limitations of the process of this invention are unexpectedly thermally stable and relatively non-corrosive in lubricant compositions used in the presence of copper metal and other sulfur-corrodible metals.

The organic sulfide produced by the method of this invention are oil soluble, extreme pressure additives for lubricating oils, transmission fluids or greases which occasion little or no corrosion to copper. The additive can be used in the conventional lubricating base media,

such as naphthenic and paraffinic mineral oils and synthetic lubricants, such as hydrocarbon fluids, glycol ether fluids, polysiloxane fluids, acetals, polyphenyl ethers, and the synthetic ester lubricants produced from monohydric alcohols and polycarboxylic acids and polyhydric alcohols, such as trimethylolpropane and pentaerythritol, and carboxylic acids having from to about 20 carbon atoms.

The following examples presented as an illustration of this invention and are not considered limiting any aspect thereof.

PREPARATION OF PRODUCT

Into a 5-liter reaction flask was added 2,025 grams (15.0 moles of sulfur monochloride) and the contents were heated to 45° C. Through a sub-surface gas sparger, 1,468 grams (26.2 moles of isobutylene gas) was fed into the reactor over a 5-hour period. The temperature was maintained between 45° and 50° C. At the end of the sparging, the reaction flask had an increase in weight of 1,352 grams.

Into a 12-liter reaction flask were added 2,150 grams (16.5 moles) of 60 percent flake sodium sulfide, 240 grams (7.5 moles) sulfur, and a solution of 420 ml of isopropanol in 4,000 ml. of water. The contents were heated to 40° C. The adduct of the sulfur monochloride and isobutylene previously prepared was added over a ¼-hour period while permitting the temperature to rise to 75° C. The reaction mixture was refluxed for 6 hours, and afterward the mixture was permitted to form into separate layers. The lower aqueous layer was discarded. The upper organic layer was mixed with 2 liters of 10 percent aqueous sodium hydroxide and the mixture was refluxed for 6 hours. The organic layer was again removed and washed with 1 liter of water. The washed product was dried by heating at 90° C. and 30 mm Hg pressure for 30 minutes. The residue was filtered through diatomaceous earth filter aid to give 2,070 grams of a clear yellow-orange liquid.

The analysis of this product was as follows:

% Sulfur	46.4
% Chlorine	0.2

EVALUATION OF PRODUCT

1. Load Carrying Test

The product of Example 1 was evaluated in the SAE Load Carrying Test as a lubricating oil additive. In this a gear lubricant is measured under high speed shock conditions. The oil composition, using a SAE-90 solvent refined Mid-Continent oil as the base oil, is placed in the SAE test machine as a lubricant for two steel test rings. These rings are rotated to produce a combination of rolling and sliding actions while a gradually increasing load is mechanically applied. The tests were conducted at 500 rpm. The results are reported as lbs. (scale reading) at the point at which scoring or seizure occurs signifying the failure of the lubricant. The maximum reading on the scale is 460 lbs.

The results are tabulated below

Composition	Failure load (lbs)
	500 rpm
Base Oil	25, 50
Base Oil 4.3% Product of Example 1	460, 460

2. Corrosion and Stability Tests

The oil sample, tested in the previous test, was subjected to two high temperature tests. In one test, the sample is heated to 250° F. and held at that temperature for 3 hours, in the presence of copper metal. At the end of a 3-hour period, the surface of the copper is observed for corrosion. In the second test, the sample lubricant is splashed onto a tared aluminum panel heated to 500° F. A mechanical splasher throws the oil against the panel. The operation is conducted for 6 hours after which time the panel is cooled down and weighed. This test, a well-known high temperature oxidation test of oil compositions, is used to determine the tendencies of such compositions to form solid deposits when in contact with high temperature surfaces. The results of the two tests are as follows:

Test	Result
Copper Corrosion Panel Coking	2A* 1 mg wt. gain

*2 refers to a slight tarnishing of the surface; no corrosion, A means the surface is not pitted.

The sulfurized olefins of this invention are found to be useful additives for lubricating oils. They provide load carrying properties and anti-oxidant properties. Moreover, they are stable at high temperatures and cause little or no corrosion to copper. In addition, they are compatible with the other additives normally used in lubricating compositions, such as anti-oxidants, extreme pressure agents, viscosity control agents, detergents and the like.

The description and disclosure of the preferred embodiments of this invention are not to be construed as presenting limitations of the invention except as defined and limited in the following claim.

I claim:

1. A polysulfurized olefin produced by the steps of (1) reacting sulfur monochloride with from 1 to 2 moles of isobutylene per mole of said sulfur monochloride at a temperature of from 20° C to about 80° C, (2) reacting this product with an alkali metal monosulfide and free sulfur, wherein the ratio of the moles of alkali metal monosulfide to the gram-atoms of free sulfur is from about 1.8 to about 2.2:1, and (3) reacting this product with an aqueous solution containing from about 5 to about 20 percent of an alkali metal hydroxide for a time sufficient to reduce the chlorine content below about 0.5 percent.

2. The polysulfurized isobutylene of claim 1 wherein the mole ratio of olefin to sulfur monochloride is from about 1 to 2:1.

3. The polysulfurized olefin of claim 2 wherein the mole ratio of isobutylene to sulfur monochloride is from about 1.25 to 1.8:1.

4. The polysulfurized olefin of claim 1 wherein the polysulfurized olefin contains from about 40 to about 60 percent of sulfur.

5. The polysulfurized olefin of claim 4 wherein the polysulfurized olefin contains from about 46 to about 50 percent of sulfur.

6. The polysulfurized olefin of claim 1 wherein the polysulfurized olefin is produced by reacting sulfur

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monochloride with from 1.25 to 1.8 moles per mole of sulfur monochloride of isobutylene, reacting the product of that reaction with an alkali metal monosulfide, and 0.5 gram atoms of free sulfur per mole of metal monosulfide.

7. The polysulfurized olefin of claim 1 wherein the alkali metal hydroxide is sodium hydroxide.

8. The polysulfurized olefin of claim 1 wherein the alkali metal monosulfide is sodium sulfide.

6

9. The polysulfurized olefin of claim 1 wherein the mole ratio of alkali metal monosulfide to sulfur monochloride-olefin product is from about 0.8 to about 1:2.

10. The polysulfurized olefin of claim 1 wherein the alkali metal monosulfide and sulfur are reacted with the sulfur monochloride-olefin product in the presence of a water-soluble alcohol.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,697,499 Dated October 10, 1972
Inventor(s) Herbert Meyers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 2, line 48 "It believed" should be -- It is believed --. In column 4, Claim 1, line 54 and 55 "The polysulfurized isobutylene of claim 1 wherein mole ratio of olefin" should be -- The polysulfurized olefin of claim 1 wherein the mole ratio of isobutylene --.

Signed and sealed this 20th day of February 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents