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SULPHURIZED HYDROCARBON
DERIVATIVES

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This invention relates to new sulphurized hydrocarbon derivatives and more particularly refers to phosphite esters of sulphurized higher molecular weight unsaturated alcohols and processes for their production and use.

Hydrocarbon derivatives containing both sulphur and phosphorus are well known in the art. Thioesters of phosphorus obtained by reacting a thiol and a phosphorus halide have been used as lubricant stabilizers and corrosion inhibitors. These products, however, have the disadvantage that they hydrolyze readily and form compounds which have an objectionable odor and a tendency to blacken metallic surfaces. Other sulphur- and phosphorus-containing hydrocarbon derivatives have been prepared by reacting alcohols and phosphorus pentasulphide, but these products are relatively unstable too and have a tendency to blacken any copper surfaces with which they may come in contact. Still other derivatives of a somewhat similar type have been produced by sulphurizing glycerides. These products are of value as stabilizers for lubricating oils but to be practicably effective they have to be employed in large quantities. An additional disadvantage of many hydrocarbon derivatives of this type is that they do not blend well with mineral oils since they are frequently quite viscous or not entirely soluble in the oil and do not impart much improvement in film strength. Some of these derivatives are also irritating to the skin, so that they cannot be used in operations wherein they would come in contact with the human body—for example, in cutting oils.

It is an object of this invention to overcome the foregoing disadvantages of prior art hydrocarbon derivatives containing sulphur and phosphorus. A further object is to produce a new class of hydrocarbon derivatives which are stable, relatively free from objectionable odors and similar undesirable properties. A still further object is to produce hydrocarbon derivatives which are particularly adapted for use as stabilizers for lubricants. A still further object is to produce compounds which blend readily with mineral oils and which may be added thereto in small quantities to improve their valuable properties. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained in accordance with the present invention wherein phosphite esters of sulphurized unsaturated alcohols containing at least five carbon atoms in the molecule are produced. In a more restricted sense, this invention pertains to phosphite esters of sulphurized unsaturated alcohols wherein said alcohols contain from eight to eighteen carbon atoms in the molecule. In a still more restricted sense,

this invention pertains to phosphite esters of a mixture of sulphurized unsaturated alcohols in which the alkenyl groups correspond in carbon content and composition to the fatty acids occurring naturally in sperm oil. In a still more restricted sense, this invention pertains to processes for the production and use of the foregoing and related compounds.

The invention may be understood more readily by a consideration of the following illustrative examples wherein the quantities are stated in parts by weight.

Example I

In an open vessel provided with mechanical agitation 335 parts of the mixture of unsaturated alcohols obtained by the sodium reduction of sperm oil and 40 parts of flowers of sulphur are heated for 3 hours at 150° C. After cooling, 800 parts of benzene are added together with 99 parts of pyridine. After mixing 57.3 parts of phosphorus trichloride, dissolved in 80 parts of benzene, is added slowly with vigorous agitation, the temperature being maintained at 30° C. After agitating two hours, the mixture is warmed one-half hour and filtered. The filtrate is stirred with a small amount of sodium carbonate monohydrate, filtered, and the solvent evaporated under reduced pressure. A reddish, fluid, residue is obtained weighing 380 parts and containing 10.3% sulphur and 3.2% phosphorus. It is readily soluble in organic solvents such as benzene, toluene, kerosene, gasoline, lubricating oils, butyl alcohol, and carbon tetrachloride. Solutions of the material in petroleum hydrocarbons do not deposit sulphur on standing and copper strips placed in the solutions do not become discolored on warming for some time.

Example II

This preparation is conducted in the same manner as in Example I using 134 parts of the alcohol and 32 parts of sulphur, 23 parts of phosphorus trichloride, and 40 parts of pyridine. The final product contains 3.7% phosphorus and 8.1% sulphur.

Example III

The preparation is performed in the same manner as in Example I except that 80 parts of sulphur is used in the initial mixture. The final product is a greenish-red fluid containing 18.1% sulphur and 2.9% phosphorus. It is readily soluble in many organic solvents and does not deposit sulphur on standing. It has a mild odor similar to that of the alcohols from which it is derived.

The effectiveness of these materials in stabilizing lubricating oils against formation of corrosive products and against deposition of sludge is

demonstrated in an engine test, the results of which are given in the following example.

Example IV

The test is conducted on a 1941 model six-cylinder Chevrolet engine, mounted on a block, and operating at a speed of 3150 R. P. M. (equivalent to a road speed of 60 miles per hour) against a load of 35 brake horsepower (equivalent to that obtained in road operation) applied by means of a dynamometer for a period of 66 $\frac{2}{3}$ hours (corresponding to road operation for 4,000 miles). At the end of the run, the engine is disassembled, inspected, and rated as to cleanliness. In the system of cleanliness rating employed a clean engine would score 100 points. Points are deducted from this score based on the quantity and quality of sludge and other deposits in various parts of the engine. An engine with a score of about 50 points is so badly fouled as to be in imminent danger of mechanical failure due to impaired lubrication circulation caused by the presence of large amounts of sludge or other deposits.

In the following tests an oil temperature of 250° F. and a jacket temperature of 160° F. are employed.

Additive	Concentration of additive, per cent by weight	Oil condition	Engine score	Copper-lead corrosion, g./bearing
None—control.....		Bad.....	52	0.8 $\frac{1}{2}$
Product from Example I.....	1.00	Good.....	88	0.16
Product from Example III.....	0.57	Fair.....	72	0.16

The stabilizing effectiveness of these products is also shown strikingly in the well known Underwood test. In this test oil at 325° F. is sprayed over a section of bearing metal. Means are provided for recirculating the sprayed oil so that a given quantity is used in a given test, thus simulating service conditions in an engine. In order to accelerate deterioration of the oil, a copper strip catalyst is placed in the oil stream. The bearing metal is removed and weighed at intervals to determine extent of corrosion, and samples of the oil are removed and analyzed at intervals to determine the extent of oil deterioration. The method used is essentially that described in a pamphlet dated August 1, 1938, of the Research Laboratories Division of the General Motors Corp., entitled "Underwood Oxidation Testing Apparatus," with the exception that the apparatus is thoroughly cleaned before each test and that the oil contained 70 parts per million of dissolved iron (as oleate).

Results of Underwood Test (15 hrs.)

	Control oil	Oil+0.92% Example II	Oil+1.84% Example II
Copper-lead corrosion mg. loss per bearing.....	643.6	12.0	6.0
Viscosity rise at 210° F. Say-bolt seconds.....	450.8	2.9	0.3
Total sludge, mg/10 g. oil.....	1,767.4	65.4	18.4
Asphaltenes, mg/10 g. oil.....	1,759.6	24.3	3.4
Neutralization number mg/KOH/g. oil.....	39.8	3.2	0.7

In addition to their over-all lubricant stabilizing effect these products improve the load-carrying capacity of a mineral oil as shown by the data in the following table, the tests being con-

ducted on a Cornell friction tester. This method of test has been described in U. S. Patent 2,279,560, page 3, right hand column, line 62 ff.

Additive	Concentration, per cent by weight	Jaw load at seizure
None—control.....		800-900
Product from Example I.....	1.0	1,000
Product from Example II.....	1.0	1,350

It is to be understood that the foregoing examples are descriptive merely of a few of the many modifications embraced within the scope of this invention. They may be varied widely with respect to the individual reactants, the amounts thereof, and the conditions of reaction, without departing from the scope hereof.

It is contemplated that any alcohol containing five or more carbon atoms may be used in accordance with this invention. Where the alcohol is saturated, the sulphurizing treatment should be carried out under such conditions that dehydrogenation of the alcohol takes place. For most satisfactory results it is advisable to select alcohols or mixtures thereof which initially contain a substantial amount of olefinic bonds. These alcohols are advisably unsaturated, aliphatic primary or secondary alcohols. Normal primary unsaturated alcohols containing from eight to eighteen carbon atoms are preferred for most purposes. The alcohol may likewise contain more than one hydroxyl group, although monohydric alcohols are generally of optimum value herein. A representative few of the many alcohols falling within the foregoing categories are: 9,10-octadecenyl, linoleyl, hexadecenyl, ricinoleyl, undecylenyl, terpen, erucyl, 4-hexenyl, 5-heptenyl, 6-octenyl, 6-nonenyl, 8-decenyl, and 4-phenylolel. In place of the pure alcohols mixtures of alcohols such as are obtained by the carboxyl reduction of fish oils or unsaturated fatty acids and esters may be used.

Unsaturated alcohols suitable for use herein may also be obtained by chlorination of paraffin wax followed by dechlorination and hydrolysis with aqueous alkali.

Pure alcohols or mixtures of two or more alcohols, or mixtures of alcohols with non-alcoholic materials may be used in accordance with this invention, provided a substantial amount of unsaturated alcohols containing five or more carbon atoms are present therein.

The alcohol is sulphurized in accordance with well known chemical technique. This may be accomplished, for example, by treatment with sulphur at elevated temperatures. The temperature of sulphurization may range from about 120° C. to about 180° C., although for optimum results this temperature range is usually between about 140° C. and 160° C. Sulphurization is preferably carried out at atmospheric pressure, although pressures above or below atmospheric are suitable. The foregoing treatment is generally completed within a period of two to six hours. Since the temperature and time of treatment will depend to a considerable extent upon the alcohol or alcohol mixture undergoing treatment, it is to be understood that the foregoing limits are not critical but merely indicative.

The amount of sulphur used in the sulphurization may vary widely, depending upon the material undergoing sulphurization, the conditions of sulphurization, and the particular characteristics which it is desired to obtain in the resulting prod-

ucts. As a general rule, it may be stated that about two molecules of sulphur should be used per olefinic linkage in the unsaturated alcohol.

The sulphurized derivative is converted into a phosphorus-containing compound by treatment with a trivalent phosphorus esterifying agent. Agents which are particularly adapted for this purpose are the phosphorus halides and phosphorus acids, although the invention is not restricted thereto. The preferred esterifying agent is phosphorus trichloride. The amount of this compound used may vary within wide limits depending upon the sulphurized alcohol undergoing treatment and the properties which it is desired to impart to the resulting products.

Esterification with the trivalent phosphorus esterifying agent is generally accomplished at temperatures below 50° C., although it should be understood that this temperature is not critical. This esterification is advisably conducted in the presence of an acid acceptor and an organic solvent. Among the many compounds of this type which are suitable for use mention may be made of acid acceptors such as dimethylaniline, calcium carbonate, sodium carbonate, and pyridine. If an acid acceptor is not used the reaction is advisably conducted under a slight vacuum in order to facilitate removal of hydrogen halide, as it is formed. Esterification is advisably carried out in the presence of a normally liquid, volatile, organic solvent such as dipropyl ether, dibutyl ether, xylene, toluene, kerosene, cyclohexane, decahydronaphthalene, naphtha, etc. It is also possible to use an excess of organic acid acceptor which may perform the additional function of serving as a solvent for the reaction. An organic acid acceptor of this type is dimethylaniline.

Products produced in accordance with this invention may be employed with petroleum hydrocarbons generally. They are particularly useful in petroleum lubricating oils and greases to improve oiliness, load-carrying capacity, resistance to sludge formation, prevention of sludge deposition, and reduction of corrosive tendencies. They may be used with gasoline, kerosene, Diesel and furnace fuel oils, or synthetic fuels such as iso-

octane of isopropyl ether to reduce the wearing of pump parts through which these fuels flow. They may be used to prevent rusting and corrosion of steel or metal surfaces through application to the surfaces either with or without a solvent. The products may be used as stabilizers and corrosion inhibitors for anti-freeze compounds. They may be used also as plasticizers and softeners for many resins and polymeric materials and may serve as lubricants for textile yarns. Furthermore, they are useful ingredients of insecticidal compositions. They form valuable addition products with various compounds such as cuprous chloride and thus may serve as carrier agents in the preparation of metallic compounds which are soluble in many organic solvents. They may be employed in cutting oils or drawing oils, etc.

By the term "petroleum hydrocarbons" is meant the various hydrocarbons of petroleum origin such as natural oils, cracked products, alkylated products, polymerized products, reformed products, and products which have been refined or treated in known manner.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Phosphite esters of a sulphurized mixture of substantially pure aliphatic unsaturated alcohols, containing from eight to eighteen carbon atoms in the molecule.

2. Phosphite esters of a sulphurized mixture of substantially pure aliphatic alcohols obtained by the carboxyl reduction of sperm oil.

3. Improved lubricating oils containing less than five per cent of the phosphite esters referred to in claim 1.

4. Improved mineral lubricating oils containing less than two percent of the phosphite esters referred to in claim 2.

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