

## UNITED STATES PATENT OFFICE

2,627,523

S-(SULFURIZED TERPENE HYDROCARBON)  
DITHIOPHOSPHORIC ACID TRIESTERS  
AND METHODS OF PRODUCING THE SAMEEdwin O. Hook, New Canaan, and Lindley C.  
Beegle, Stamford, Conn., assignors to American  
Cyanamid Company, New York, N. Y., a corpo-  
ration of MaineNo Drawing. Application August 30, 1950,  
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3 Claims. (Cl. 260—461)

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This invention relates to a class of improved antioxidant and corrosion inhibiting agents for hydrocarbon oils. More specifically, the invention is directed to the provision of sulfurized terpene esters of O,O-dithiophosphoric acid diesters, hereinafter sometimes called S-(sulfurized terpene hydrocarbon) dithiophosphoric acid triesters, as antioxidants and corrosion inhibitors for hydrocarbon lubricating oils. The invention includes the dithiophosphoric acid-sulfurized terpene esters, which are new compositions of matter; their method of preparation, and improved hydrocarbon oils containing them.

The addition of sulfurized terpenes to hydrocarbon lubricating oils has previously been suggested. Simple sulfurized hydrocarbons of this type, however, are not sufficiently powerful as antioxidants for many purposes. Attempts have therefore been made to further condense these products with phosphorous sulfides in order to increase their antioxidant power. However, the resulting products have not exhibited the degree of solubility in hydrocarbon lubricating oils that is usually desired, i. e., the product tends to separate from the oil in which it is dissolved after a few days' standing. It is a principal object of the present invention to provide a class of non-metallic antioxidants for lubricating oils which possess a high degree of antioxidant power but which are permanently soluble therein and do not separate or cause turbidity in the oil even after long periods of standing or use.

We have found that the new compounds obtained by condensing halogen-containing sulfurized terpene hydrocarbons with salts of O,O-diester of dithiophosphoric acid possess both antioxidant and corrosion inhibiting properties to a high degree. We have also found that these non-metallic compounds are easily and permanently soluble in hydrocarbon lubricating oils, including both paraffin base oils and naphthenic base oils, in amounts sufficient to inhibit oxidation of the oil and to obtain anticorrosion properties therein, i. e., in amounts of about 0.1-5% by weight. Concentrates containing up to 40-50% by weight of our new antioxidants in hydrocarbon lubricating oils can also be prepared for storage and blending with lubricating oil stocks if desired.

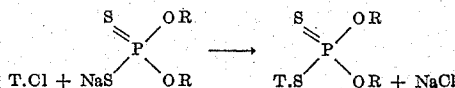
The halogen-containing sulfurized terpenes employed in preparing our new compounds are obtained by condensing a terpene hydrocarbon with a sulfur halide such as sulfur chloride (S<sub>2</sub>Cl<sub>2</sub>) or sulfur dichloride (SCl<sub>2</sub>) or the corresponding sulfur iodides, bromides or fluorides.

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This condensation may be carried out by known methods, employing, for example, from 1-2 mols of terpene for each mol of sulfur dichloride. The condensation is exothermic, and is preferably carried out at relatively low temperatures of 25-50° C., although higher temperatures up to 100° C. are sometimes employed. Theoretically, there is no limit on the temperature at which this reaction can be carried out, as sulfur monochloride, sulfur dichloride, sulfur iodide, sulfur bromide and sulfur fluoride will condense with bicyclic terpene hydrocarbons at any suitable temperature.

Terpenes sulfurized with sulfur halides are believed to contain one firmly bound atom of halogen per molecule and a second labile or more loosely bound atom of halogen. In order to impart improved heat stability to the finished products, as well as to obtain a favorable ratio of dithiophosphoric acid to terpene, we remove part or all of the loosely bound halogen. This is done by heating the sulfurized terpene at atmospheric pressure. The compounds heated to 100-120° C. lose about 25% of their chlorine or other combined halogen; when heated to 150-160° C. or higher they lose about 50%, which represents substantially all of the labile or loosely bound halogen. We prefer to conduct the dehalogenation between these two limits (i. e., between about 110-120° C. and 150-160° C.) so that the heat-treated sulfurized terpenes contain from 1 to about 1.5 molecules of combined halogen per molecule.

The halogen-containing sulfurized terpenes so prepared are condensed with salts of O,O-dithiophosphoric acid diesters. This produces an S-(sulfurized terpene hydrocarbon) dithiophosphoric acid triester. The reaction is most clearly shown by the following equation, in which T represents the molecular residue of a halogen-containing sulfurized terpene hydrocarbon and R is an aliphatic cycloaliphatic, aromatic or other ester-forming radical of the O,O-dithiophosphoric acid diester



This reaction is usually carried out in the presence of a solvent for the dithiophosphate salt used in the condensation, and preferably in the presence of a polar solvent such as water, aliphatic monohydric alcohols and the like. Other solvents such as toluene, solvent naphtha and the like may also be present if desired. In some

cases, as when preparing concentrates containing 40% or more of the nonmetallic additive, the reaction can be carried out in the presence of the lubricating oil which is the intended vehicle. This is most easily accomplished by dissolving either the O,O-dithiophosphoric acid diester salt, or preferably, the chlorine-containing sulfurized terpene in the lubricating oil and adding a suspension or solution of the other reagent in water or other polar solvent, such as in aqueous ethanol or methanol. After evaporating the solvent the chloride or other halide produced can be removed from the oil by filtration.

Any desired ratio of dithiophosphoric acid ester salt to halogenated sulfurized terpene may be employed in the above reaction from appreciable amounts (such as 0.1-0.2 mols) up to an equimolecular quantity of the dithiophosphoric acid ester salt. Larger quantities of the ester salt can of course be added to the reaction mixture, but will remain unreacted in the final product.

It will be evident that any salt of any O,O-diester of dithiophosphoric acid can be employed in this reaction, since the ester-forming groups take no part therein. Moreover, since oil solubility is imparted by the sulfurized bicyclic terpene as an ester radical, it is not necessary to use long-chain lyophilic radicals in the dithiophosphoric acid diester. For this reason, either R in the above formula may be any aliphatic radical of from one to 18 carbon atoms or more. Typical esters of this class are described in the following examples. On the other hand, it will be evident that other radicals may be employed if desired, such as phenyl or alkylphenyl radicals of from 6 to 22 carbon atoms. The O,O-dithiophosphoric acid diester salts used in preparing our new compounds are therefore the dialiphatic, including dialkyl compounds in which each R is a saturated hydrocarbon radical of 1 to 18 carbon atoms; the diaryl, in which each R is a phenyl or alkylphenyl radical of 6 to 22 carbon atoms or more, for example, the 4-propylphenyl, 4-butylphenyl, 4-octylphenyl, 2,4-diisopropylphenyl, 2,4-dibutylphenyl and 2,4-dioctylphenyl radicals or dicycloaliphatic esters of alcohols of 6 to 10 or more carbon atoms such as the dicyclohexyl ester and those obtained by the hydrogenation of naphthenic acids. Mixed esters in which one R is one of the above radicals and the other R is another one of the same or different class may also be employed if desired. The salt-forming radical may be alkali metal, ammonium, alkaline earth metal, zinc, an organic base such as aliphatic amine, pyridinium and the like, or in general, any basic salt-forming radical may be employed.

Any terpene hydrocarbon may be used in preparing the halogen-containing sulfurized materials used to condense with dithiophosphoric acid salts. The monocyclic terpenes such as the limonenes or dipentene or terpinenes may be used. All of the bicyclic terpenes may be employed. These are classified as the sabinanes and the carene, pinane and camphane hydrocarbons of the formula  $C_{10}H_{16}$ . Typical compounds of these classes are carene, sabinene and particularly alpha- and beta-pinene and sulfate turpentine in which the principal constituent is alpha-pinene. Camphene, fenchene and bornylene are other typical terpenes. As a practical matter, however, it is most convenient to employ mixtures containing these terpenes in admixture with each other or with other substances, such as the commercial mixture known as "Tenrex"

which contains 20-25% of beta-pinene and up to 5% of alpha-pinene along with 50-65% of dipentene and up to 5% cymene.

As has been explained, the reaction between the O,O-dithiophosphoric acid diester salt and the partially dehalogenated sulfurized terpene is most conveniently carried out in the presence of water, aliphatic monohydric alcohols or other polar solvents, or mixtures thereof. Reaction temperatures ranging from about 25° C. to 100° C., or to the boiling point of the solvent at atmospheric pressure if a volatile solvent is employed, may be used. The upper temperature limit of the reaction is about 120-130° C. Suitable solvents are ethanol, propanol, isopropanol, or any of the various butyl or amyl alcohols thereof. These alcohols are usually employed in admixture with water.

The condensation reaction is preferably carried out in the presence of an alkali in the reaction mixture. Any suitable inorganic alkali such as an alkali metal hydroxide or carbonate or ammonium hydroxide may be employed. Ordinarily, a quantity of alkali is added sufficient to maintain the reaction mixture neutral or alkaline at all times, the preferred pH range being from 7.0 to 8.5. In most cases the reaction is carried out under definitely alkaline conditions so that any hydrogen halide liberated during the reaction will be neutralized and any desired quantity of free alkali sufficient to accomplish this purpose may be added.

When the reaction is carried out in water the product will separate therefrom as an oily layer that can be recovered by simple decantation. When alcohols or other polar solvents are used, the S-(sulfurized terpene hydrocarbon) dithiophosphoric acid triester may be dissolved therein. In both cases, however, the desired reaction product is preferably recovered and purified by washing with hot 10-20% aqueous sodium carbonate solution or other alkali and stripping by heating under a vacuum. Stripping temperatures of 90-125° C. may be used at pressures of 20-25 mm. of mercury, which results in the removal of excess unreacted terpenes and other impurities from the reaction product.

The new non-metallic antioxidant and corrosion inhibiting agents of our invention are obtained as brownish-red viscous liquids which are soluble in toluene and in mineral lubricating oils. When hydrocarbon oils containing 0.1-2% by weight of these compounds are tested they show a very satisfactory resistance to oxidation and do not readily corrode either lead alloy or silver-cadmium bearings.

The invention will be described and illustrated in greater detail by the following specific examples.

#### Example 1

At a temperature of 45-50° C. 51.5 lbs. of  $SCl_2$  was slowly added to 136 lbs. of a commercial grade mixture of terpenes known as Tenrex and consisting of 50-65% of dipentene, 20-25% beta-pinene, 0.5% alpha-pinene, and 0-5% cymene. The mixture was then heated to 120° C. over a 2 hour period to remove approximately 25% of the combined chlorine as HCl.

The product was mixed with 450 lbs. of an aqueous solution of the sodium salt of di-(4-methyl-2-pentyl) dithiophosphoric acid (the solution contained 0.45 mol of the dithiophosphoric acid salt) and an aqueous solution consisting of 13 lbs. of  $Na_2CO_3$  in 51 lbs. of  $H_2O$ . The reaction mixture was then heated for 1.5 hours at 90° C.

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During the heating period 4 lbs. of additional  $\text{Na}_2\text{CO}_3$  was added in increments to maintain alkaline conditions.

The product layer was thereafter separated from the aqueous layer, washed twice with 13 lb. portions of  $\text{Na}_2\text{CO}_3$  in 48 lbs. of water at a temperature of  $90^\circ\text{C}$ ., after which the excess terpene was stripped off at  $110^\circ\text{C}$ . under 17 mm. of mercury. Upon filtration, 229 lbs. of a dark reddish viscous liquid was obtained. 19 lbs. of filter press blowings was recycled to a succeeding filtration batch. The product was completely soluble in mineral lubricating oil.

The product was evaluated as a lubricating oil antioxidant by dissolving 0.5% by weight thereof in an S. A. E. 30 Mid-Continent base lubricating oil together with 0.04% of iron naphthenate, based on the  $\text{Fe}_2\text{O}_3$  equivalent, and subjecting the oil to the standard Underwood Oxidation Test. In this test, 1500 cc. of the compounded oil is heated for 10 hours at  $325^\circ\text{F}$ . in an open container providing free circulation of air while portions of the oil are sprayed continuously against two freshly sanded alloy bearings. When cadmium-silver bearings were used in the test with the above oil containing the iron naphthenate oxidation catalyst but no anti-oxidant, the loss in bearing weight due to corrosion was approximately 1800 mg. The compounded sample, on the other hand, had a bearing corrosion loss of 0 and the oil increased only 8% in viscosity. In evaluating antioxidants according to the Underwood test, the maximum permissible corrosion loss is 250 mg. while the oil should not increase more than 50% in viscosity. From the foregoing test data it will be seen that the antioxidant described in the above illustrative example provided excellent protection against corrosion and oxidation.

Another portion of the above product was dissolved in Mid-Continent base S. A. E. 30 grade lubricating oil to an 0.8% solution and tested in a Chevrolet automobile engine in a 36 hour continuous run according to the Coordinating Research Council test L-4-545. The Cu-Pb bearing inserts of the engine lost 79 mg. as compared with a loss of about 2000 mg. for a control sample which contained no antioxidant. Analysis of the used oil showed that the neutralization number had increased from 0.1 to 1.2 while the Saybolt viscosity at  $100^\circ\text{F}$ . had increased only 14%, whereas the Neut. No. of the control sample increased to 6.7 while its viscosity increased more than 100%.

#### Example 2

309 grams of  $\text{SCl}_2$  was slowly added to 816 grams of the Tenrex described in Example 1. The addition was made at a temperature of  $45\text{--}55^\circ\text{C}$ . Thereafter the mixture was heated and held at approximately  $120^\circ\text{C}$ . for 1.5 hours to remove approximately 25% of the combined chlorine.

367 grams of the above terpene adduct was mixed with 285 grams of the sodium salt of diisopropyl dithiophosphoric acid in 500 grams of water. 26 grams of  $\text{Na}_2\text{CO}_3$  in 100 cc. of water was added to the mixture after which it was heated for 1.5 hours on a steam bath. The liquid product layer was allowed to separate from the aqueous portion of the reaction mixture after which the product was washed twice with 100 cc. portions of hot 20%  $\text{Na}_2\text{CO}_3$ . The excess terpene and water was then removed by stripping under vacuum at a temperature of  $95\text{--}100^\circ\text{C}$ . Upon filtration a brownish-red viscous liquid was obtained which was easily soluble in mineral lubri-

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cating oil. The Underwood Oxidation Test, at a concentration of 0.4% of this product in S. A. E. 30 grade lubricating oil, showed that the cadmium-silver bearings had suffered no corrosion and that the viscosity of the oil increased only 12%.

#### Example 3

206 grams of  $\text{SCl}_2$  was gradually added to 544 grams of beta-pinene at  $40\text{--}50^\circ\text{C}$ . The mixture was then heated for one hour at  $120\text{--}130^\circ\text{C}$ . to remove a portion of the chlorine from the reaction product. The product was then mixed with 1600 grams of an aqueous solution of the sodium salt of di-(4-methyl-2-pentyl) dithiophosphoric acid (the solution contained 1.6 mol of the dithiophosphoric acid salt). 53 grams of  $\text{Na}_2\text{CO}_3$  in 200 cc. of water was added and the mixture was heated on a steam bath for 1.75 hours. The liquid product layer was separated from the aqueous portion of the mixture and was thereafter washed twice with 200 cc. portions of 20% aqueous  $\text{Na}_2\text{CO}_3$ . Thereafter, the product was stripped under vacuum at  $95\text{--}100^\circ\text{C}$ . The product closely resembled those of the previous two examples and was equally as soluble in mineral lubricating oil.

When tested by the standard Underwood Oxidation Test at a concentration of 0.5% the oil caused no corrosion loss of the bearings and the viscosity of the oil increased 27%.

Any other O,O-dithiophosphoric acid diester of one or more branched-chain aliphatic monohydric alcohols of 3 to 18 or more carbon atoms may be used instead of the methyl isobutyl carbinol ester described above with equivalent results. Suitable diesters of this type are described in U. S. Patent No. 2,368,000, and any of the diesters described therein may be used in the form of their alkali metal, ammonium, organic base or polyvalent metal salts.

#### Example 4

206 grams of  $\text{SCl}_2$  was added slowly to 544 grams of alpha-pinene at a temperature of about  $50^\circ\text{C}$ . after which the mixture was heated for 2 hours at  $120\text{--}125^\circ\text{C}$ ., whereby 743 grams of product were obtained. 371 grams of this product was mixed with 270 grams of di-(4-methyl-2-pentyl) dithiophosphoric acid, 45 grams of water and 40 grams of  $\text{NaOH}$ . The mixture was then heated for 2 hours on a steam bath, during which time 10 additional grams of  $\text{NaOH}$  were added. 200 cc. of water were added to the reaction product to take up the sodium chloride produced during the reaction. The product was thereafter washed twice with hot aqueous  $\text{Na}_2\text{CO}_3$  after which it was stripped and filtered in a manner similar to that described in the previous examples. The product contained 5.4% of chlorine and 15.6% of sulfur and, while the material was an excellent anticorrosion agent for internal combustion engine lubricating oils, it was also an excellent extreme pressure additive. When tested by the standard Underwood Oxidation Test at 0.5% concentration, the bearings suffered no corrosion loss and the viscosity of the oil increased only 7%.

#### Example 5

The procedure of Example 1 was repeated with the exception that 544 grams of the terpene mixture was employed and 270 grams of  $\text{S}_2\text{Cl}_2$  was substituted for the sulfur dichloride. Underwood Oxidation Test results, at a concentration of 0.625% by weight of the above described additive

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together with 0.04% of iron naphthenate, showed a bearing corrosion loss of 0 and an oil viscosity increase of 31%.

#### Example 6

309 grams of  $\text{SCl}_2$  was added gradually to 816 grams of dipentene at a temperature of  $30^\circ\text{C}$ . after which the mixture was heated to  $150^\circ\text{C}$ . and held at this temperature for one hour. 1027 grams of product was obtained.

348 grams of this material was mixed with 1130 grams of an aqueous solution of the sodium salt of di-(4-methyl-2-pentyl) dithiophosphoric acid containing about 1.2 mols of salt. The mixture was heated on a steam bath for 2 hours, after which it was washed with two 125 cc. portions of 20% aqueous  $\text{Na}_2\text{CO}_3$ . After separation of the product layer, stripping to remove excess terpene, and filtering, 422 grams of a reddish-brown viscous liquid product was obtained.

When tested by the standard Underwood Oxidation Test at a concentration of 0.625% by weight, the bearings suffered no corrosion loss while the viscosity of the oil increased only 14%.

#### Example 7

120 parts by weight of cetyl alcohol and 35 parts by weight of  $\text{P}_2\text{S}_5$  were mixed and reacted at  $95^\circ\text{C}$ . for 2 hours. The product was dissolved in a mixture of 20 parts ethanol and 40 parts toluol and neutralized by the addition of 5 parts of KOH.

309 grams of  $\text{SCl}_2$  was reacted with 816 grams of dipentene at a temperature of  $45\text{--}50^\circ\text{C}$ ., after which the product was heated at  $120^\circ\text{C}$ . for 1.5 hours. Approximately 40% of the combined chlorine was released.

367 grams of this product was mixed with an alcoholic solution containing about 0.9 mol of the above described cetyl alcohol- $\text{P}_2\text{S}_5$  reaction product and 25 grams of  $\text{Na}_2\text{CO}_3$  in 100 cc. of water. The mixture was then heated on a steam bath for 1.5 hours, after which the product was stripped to remove the solvent. The residue was taken up in toluene and then washed with aqueous  $\text{Na}_2\text{CO}_3$ . The product obtained after removing the toluene was easily soluble in mineral lubricating oil and exhibited good corrosion inhibiting characteristics.

#### Example 8

160 parts by weight of dioctylphenol and 30 parts by weight of  $\text{P}_2\text{S}_5$  were reacted at about  $125\text{--}150^\circ\text{C}$ . for 2 hours. The product was thereafter dissolved in a mixture of 200 parts of ethanol and 400 parts of toluol and neutralized by the addition thereto of 6 parts of NaOH in 90% ethanol.

367 g. of the product obtained by reacting  $\text{SCl}_2$  with dipentene and dechlorinating according to the procedure set forth in Example 7 was mixed with a quantity of the above described solution containing 0.8 mol of the dioctylphenol- $\text{P}_2\text{S}_5$  reaction product, and 25 g. of  $\text{Na}_2\text{CO}_3$  in 100 cc. of water was added thereto. The mixture was then heated on a steam bath for two hours after which the water layer was removed by decantation. The

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product was then washed with aqueous sodium carbonate, separated and stripped to remove the solvent and excess terpene. A clear, reddish-brown oil-soluble material was obtained.

#### Example 9

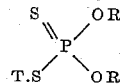
231 g. of diisopropyl dithiophosphoric acid was added slowly to a slurry of 100 g. of  $\text{Ca}(\text{OH})_2$  in 1 liter of water. The excess lime was filtered off giving a neutralized product which was a clear light yellow aqueous solution of calcium diisopropyl dithiophosphate.

Sulfur dichloride was reacted with beta-pinene in the same proportions and according to the procedure set forth in Example 3, resulting in 731 g. of product. To 365 g. thereof was added the aqueous solution of dithiophosphate described above. This mixture was heated on a steam bath for 2 hours during which time additional small portions of lime were added to maintain the reaction under slightly alkaline conditions.

The oily product layer was separated from the aqueous layer, washed twice with 100 cc. portions of hot 20% aqueous sodium carbonate solution, stripped, and filtered. 427 g. of a dark red oil-soluble product was obtained.

What we claim is:

1. An S-(sulfurized terpene) O,O-dialkyl-dithiophosphate having the formula



in which T is the residue of a sulfurized terpene hydrocarbon and each R is an aliphatic radical of from 1 to 18 carbon atoms.

2. A method of producing an S-(sulfurized terpene hydrocarbon) dithiophosphoric acid triester which comprises reacting from 1 to 2 mols of a terpene hydrocarbon with one mol of a sulfur halide, heating the reaction product to  $110\text{--}160^\circ\text{C}$ . for a time sufficient to expel about 25-50% of its combined halogen, mixing the product so obtained with a salt of an O,O-dithiophosphoric acid diester and heating the mixture until an S-(sulfurized terpene hydrocarbon) dithiophosphoric acid triester is obtained.

3. A method according to claim 2 in which the partially dehalogenated sulfurized terpene is reacted with a salt of an O,O-dialkyl dithiophosphoric acid in which each alkyl radical contains from 1 to 18 carbon atoms.

EDWIN O. HOOK.  
LINDLEY C. BEEGLE.

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