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TERPENE-PHOSPHOROUS PENTASULFIDE-
SULFUR LUBRICATING OIL ADDITIVE

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The present invention relates to a novel class of additives for hydrocarbon lubricating oils. It relates more particularly to a class of phosphorous and sulfur-containing compounds which have been found to be particularly useful as anti-oxidants and anticorrosion agents for hydrocarbon oils. The invention includes the compounds themselves, the method of their preparation, and their use as hydrocarbon lubricating oil additives.

The art has recognized that phosphorous and sulfur-containing compounds are, in general, effective in preventing the oxidation of highly refined hydrocarbon lubricating oils in internal combustion engines and in preventing the corrosion of the moving engine parts. The industry has previously employed lubricating oil additives prepared from various phosphorous and sulfur-containing compounds such as phosphorous pentasulfide, phosphorous sesquisulfide, and the like compounds. The additives have usually consisted of neutral metal salts of the products of reaction of these phosphorous and sulfur-containing compounds with various organic materials. For example, phosphorous pentasulfide has been alkylated, or reacted with various phenolic bodies, and the reaction products have been neutralized with metal oxides or hydroxides in the preparation of useful lubricating oil additives.

More recently, it has also been suggested that a useful class of lubricating oil additives might be prepared by reacting various terpenes with phosphorous pentasulfide. In most instances these reaction products have been further condensed with aliphatic and/or aromatic compounds. In general, this type of additive has been said to provide satisfactory protection against oxidation of hydrocarbon lubricating oils under normal operating conditions of internal combustion engines.

I have discovered that a novel class of hydrocarbon lubricating oil additives which possess greatly improved antioxidant and anticorrosion properties may be prepared by reacting phosphorous pentasulfide and various bicyclic terpenes with sulfur or a sulfurizing agent. The additional reacted sulfur in my novel additives greatly increases the desirability thereof over the prior art additives by virtue of their improved antioxidant and anticorrosion properties. The products, as will hereinafter be shown, provide a much greater degree of protection in the lubrication of internal combustion engines by preventing excessive corrosion of the moving parts and by substantially eliminating oxidation of the lubricants employed therein.

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It has been found that any of the bicyclic terpenes, namely those bicyclic hydrocarbons having the general formula $C_{10}H_{16}$, may be used in preparing the novel lubricating oil additives of the present invention. For example, satisfactory terpenes include alpha-pinene, beta-pinene, camphene, bornylene, nopinene (isomeric beta-pinene), fenchene, thujene, sabinene, carene, and the like bicyclic terpenes. The ordinary commercial grades of turpentine, most of which contain 85% or more of alpha-pinene, are also included within the scope of the term bicyclic terpenes as employed in the present invention.

In preparing this novel class of lubricating oil additives, the selected terpene may be reacted with phosphorous pentasulfide and an additional sulfur-providing compound under relatively elevated temperatures and under atmospheric pressure. Ordinarily, the other components are added to the terpene constituent since the bicyclic terpenes are commonly liquids. While there is no upper limit as to the amount of terpene which may be employed, other than that of economic practicability, it is usually advantageous to employ only a small excess of terpene over the stoichiometric requirement to facilitate handling of the reaction product. For example, while only about 4 mols of terpene can be reacted with one mol of phosphorous pentasulfide, it has been found that 6 mols of terpene will provide sufficient liquid vehicle to permit easy handling of the reaction product.

While various sulfurizing agents may be employed in my reaction, elemental sulfur is the preferred material since its use eliminates the necessity of removing contaminating by-products or unreacted materials. It has been found that the amount of sulfur which may be reacted with the selected terpene and phosphorous pentasulfide is within the range of from about 0.5 mol to about 3 mols for each mol of P_2S_5 present. While amounts smaller than 0.5 mol per mol of P_2S_5 may be used, the increase in antioxidant properties of the reaction product is not sufficiently substantial to be of economic desirability. On the other hand, although the presence of relatively large amounts of sulfur in the lubricating oil additives is sometimes desirable, the presence of more than about 3 mols thereof for each mol of P_2S_5 causes crystalline material to settle out of the lubricating oil additive upon storage.

A primary feature of the present invention therefore, resides in the reaction of about 4 mols of a bicyclic terpene with one mol of phosphorous

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pentasulfide and with from about 0.5 mol to about 3 mols of sulfur. If desired, the sulfur, P_2S_5 , and terpene may be reacted together. However, it has also been found that the terpene and P_2S_5 may be first reacted, and then the sulfur may be added and the mixture further reacted. Solvent extraction of the final reaction product has shown that the sulfur has reacted with the other components and is not merely in physical combination therewith.

The reaction between the terpene, P_2S_5 , and sulfur is mildly exothermic and may be easily carried out by heating the components to from about 80° C. to about 90° C. and thereafter controlling the reaction temperature as desired according to the particular type of equipment employed. When an open reaction vessel is employed under atmospheric conditions, it is preferable that the reaction temperature be maintained below about 160° C. in order to prevent excessive evaporation of the terpene. On the other hand, where reflux equipment is used, superatmospheric pressures and more elevated temperatures may be resorted to if it is so desired. The reaction products in either instance are normally dark colored, relatively viscous liquids which are readily soluble in hydrocarbon lubricating oils. Although numerous of the common organic solvents may be employed, as hereinbefore stated it is preferable to use an excess of the particular terpene employed in order to facilitate handling of the components during and subsequent to the reaction.

The novel lubricating oil additives of this invention may be employed in lubricating oils in amounts of from about 0.25% to about 2-3% or more, depending on the particular lubricating oil employed and its tendency to oxidize under use in internal combustion engines. However, it has been found that ordinarily the use of from about 0.5% to about 1.25% of the additive, by weight, entirely satisfactorily inhibits oxidation of most lubricating oils. My novel additives may be employed alone or in conjunction with other antioxidants or detergents. For example, antioxidant compositions which have been found to be particularly suitable for use with the terpene- P_2S_5 -sulfur reaction products include the metal salts of esters of dithiophosphoric acids such as barium dioctyl dithiophosphate, zinc dihexyl dithiophosphate, barium didodecyl dithiophosphate, and the like metal dialkyl dithiophosphates. Detergents which are particularly suitable include the metal salts of petroleum sulfonates such as calcium petroleum sulfonate, and the like, alkylated aromatic sulfonates such as calcium or barium dodecyl phenyl sulfonate, and the like; and metal salts of phenol sulfides and disulfides such as calcium, barium, and zinc salts of dioctyl phenol sulfide, diamyl phenol sulfide, and barium and calcium meta-, ortho-, and para-octyl phenol sulfides.

The invention will be further illustrated by the following specific examples. It should be understood, however, that although these examples may describe certain specific features of the invention, they are given primarily for purposes of illustration and the invention, in its broadest aspects, is not limited thereto.

EXAMPLE 1

To 408 grams (3 mols) of alpha-pinene, with stirring, was added 111 grams (0.5 mol) of P_2S_5 and 32 grams (1 mol) of sulfur. The mixture was heated for 2.5 hours at approximately 125°

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C. Thereafter, 300 grams of SAE 10 grade hydrocarbon lubricating oil and 10 grams of a diatomaceous earth filter aid was added to the reacted material, after which the excess alpha-pinene was stripped off at a temperature of 125° C. and 12-15 mm. Hg. The oil concentrate was then filtered. To the product, which weighed 410 grams, was added 110 grams additional SAE 10 grade hydrocarbon lubricating oil to produce a 50% concentrate in oil of the product. The reaction product contained 3.6% of phosphorous and 14.0% of sulfur.

A sample of the product was tested as an antioxidant by the Underwood corrosion test using cadmium-silver alloy bearings as test material. A 1500 cc. sample of a Mid-Continent base lubricating oil of SAE 30 grade containing 0.4% by weight of the additive and 0.04% of iron naphthenate, based on the Fe_2O_3 equivalent, as oxidation catalyst was heated for 10 hours at 325° F. while continuously spraying portions of the oil against two freshly sanded alloy bearings, the apparatus being so constructed as to permit free circulation of air. The total bearing loss was 4 milligrams, whereas the loss with a sample of the same oil containing the same quantity of iron naphthenate but no antioxidant was 1236 milligrams, while the oil viscosity increased over 300%. A sample containing a similar quantity of a P_2S_5 -alpha-pinene reaction product prepared as described above but with no additional sulfur had a total bearing loss of 495 milligrams and a viscosity increase of 79%.

EXAMPLE 2

To 408 grams (3 mols) of alpha-pinene, with stirring, was added 111 grams (0.5 mol) of P_2S_5 and 8 grams (0.25 mol) of sulfur. The mixture was heated to 120-125° C. and maintained at a temperature below 143° C., the heating being continued for a period of 2.5 hours. Thereafter the reaction product was diluted with light grade, refined mineral lubricating oil, stripped, filtered, and prepared as a 50% concentrate in oil as described in Example 1. The product weighed 357 grams and contained 4.36% phosphorous and 12.46% of sulfur and was readily soluble in hydrocarbon lubricating oils.

EXAMPLE 3

To 408 grams (3 mols) of alpha-pinene, with stirring, was added 111 grams (0.5 mol) of P_2S_5 and 48 grams (1.5 mol) of sulfur. The mixture was heated for 2.5 hours at 120-125° C. Thereafter, the reaction product was diluted with mineral lubricating oil, stripped, filtered, and prepared as a 50% concentrate in oil according to the procedure described in Example 1. The product weighed 424 grams and contained 3.67% of phosphorous and 15.1% of sulfur.

A sample of the product was added to a Mid-Continent base SAE 30 grade lubricating oil to a 0.4% solution of the additive. The bearing corrosion loss was slightly greater than 1 milligram and the treated oil increased 19.5% in viscosity when the oil was tested as described in Example 1. A control sample of the product of reaction of P_2S_5 and alpha-pinene had a bearing corrosion loss of 2844 milligrams when tested in a similar fashion, while the viscosity of the oil increased 175%.

EXAMPLE 4

Four samples were prepared as follows: Alpha-pinene was charged to a glass lined kettle and

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heated to about 115–120° C. P_2S_5 and sulfur were dry mixed and added to the heated pinene over a relatively extended period of time to prevent loss of starting materials by virtue of the exothermic reaction. The mixture was thereafter heated until reaction was substantially complete. Then a light grade (SAE 10), highly refined lubricating oil was added to the product for convenience in subsequent handling, after which the excess alpha-pinene was stripped off under vacuum at about 100–140° C. Additional SAE 10 grade hydrocarbon oil was then added to prepare a 50% concentration of the product in oil and the concentrate was filtered. The conditions under which these four samples were prepared are tabulated below in Table I.

Table I

Sample No.	Quantity of Reactants, Pounds			P_2S_5 -S Addition Temp., °C.	Average Reaction Temp., °C.	Reaction Time, Minutes	Stripping Time, Minutes	Yield of Product, Lbs.
	Alpha-Pinene	P_2S_5	S					
A-----	81.6	22.5	6.4	120	114	110	105	82
B-----	81.6	22.5	6.4	115	114	165	70	81
C-----	81.6	22.5	6.4	117	129	245	90	85
D-----	3,920	1,067	307.5	119	155-160	240	220	4,560

The above samples were tested by incorporation in a Mid-Continent base lubricating oil of SAE grade 30 in amounts of 0.75% to 1.0% by weight.

The treated oil was subjected to actual operating conditions in a Chevrolet automobile engine for a 36 hour continuous run, the engine being run at 3,150 R. P. M. under a load of 30 brake horsepower with a crankcase temperature of 280° F. and a jacket temperature of 180–200° F. The engine was thereafter dismantled and examined for bearing corrosion, and the oil was tested for viscosity and neutralization number increase. The neutralization number was determined as the number of milligrams of KOH required to exactly neutralize one gram of oil containing the above additives. Test results were as follows:

Table II

Sample No.	Concentration, percent by weight		Bearing/Corrosion, gm./l. bearing	Neut. No.		Percent Viscosity increase at 100° F.
	Terpene- P_2S_5 -S	Detergent ¹		New	Used	
Control-----	0	0	2.677	neut.	2.7	41
A-----	1.0	0	0.017	0.1	1.3	22
B-----	0.8	0	0.028	0.1	1.4	30
C-----	0.8	0	0.016	0.1	1.6	28
D-----	0.8	0	0.039	0.1	1.8	31
B-----	1.0	2.0	0.033	0.6	0.7	6
B-----	0.5	2.8	0.084	0.9	0.9	13
B-----	0.8	0.8	0.029	0.2	0.7	12

¹ The detergent employed was a barium salt of an alkylated phenol sulfide.

EXAMPLE 5

To 161 gram of camphene, with stirring, was added 44 grams P_2S_5 and 12.3 grams of sulfur. The mixture was heated to 120°–130° C. and maintained at this temperature for 2.5 hours. Thereafter the reaction product was diluted with SAE 10 grade mineral lubricating oil, stripped at 135° C., filtered, and prepared as a 50% concentrate in oil as described in Example 1.

A sample of the product was added to a Mid-Continent base SAE 30 grade lubricating oil to a 1.0% solution of the additive. The bearing corrosion loss was 0.0 milligram when the oil was

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tested as described in Example 1, while the bearing corrosion loss of a control sample of oil containing no additive was 1600 milligrams.

EXAMPLE 6

To 408 grams of beta-pinene, with stirring, was added 111 grams of P_2S_5 and 48 grams of sulfur. The mixture was heated to 80–90° C. and maintained at a temperature not greater than about 120–130° C. for 2.5 hours. Thereafter the reaction product was diluted with SAE 10 grade mineral lubricating oil, stripped at 135° C., filtered and prepared as a 50% concentrate in oil as described in Example 1.

A sample of the above product was added to a Mid-Continent base SAE 30 grade lubricating oil

to a 1.0% solution of the additive. The bearing corrosion loss was 0.0 milligram when the oil was tested as described in Example 1, while the bearing corrosion loss of a control sample of oil containing no additive was 1600 milligrams.

EXAMPLE 7

To 408 grams of steam distilled turpentine was added 111 grams of P_2S_5 and 32 grams of sulfur. The mixture was heated and maintained at a temperature of 120–130° C. for 2.5 hours. Thereafter, the reaction product was diluted with SAE 10 grade mineral oil, stripped at 130° C., filtered and prepared as a 50% concentrate in oil.

A sample of the product was added to a Mid-Continent base SAE 30 grade lubricating oil to 0.75% solution of the additive. The bearing corrosion loss was 37 milligrams when the oil was tested as described in Example 1. The viscosity of the oil increased 110% during the test period while the neutrality number increased from 0.1 to 4.0.

I claim:

1. A method of preparing a hydrocarbon lubricating oil antioxidant which comprises simultaneously reacting together a bicyclic terpene, phosphorous pentasulfide, and elemental sulfur at a temperature range of from about 115° C. to about 130° C. for a period of time not substantially exceeding four hours, the reactants being employed in the proportion of at least about 4 mols of the bicyclic terpene and from about 0.5 to about 3 mols of sulfur for each mol of phosphorous pentasulfide.

2. A method of preparing a hydrocarbon lubricating oil antioxidant which comprises simultaneously reacting together alpha-pinene, phosphorous pentasulfide, and elemental sulfur at a temperature range of from about 115° C. to about 130° C. for a period of time not substantially exceeding four hours, the reactants being employed in the proportion of at least about 4 mols of alpha-pinene and from about 0.5 to about 3 mols of sulfur for each mol of phosphorous pentasulfide.

3. A method of preparing a hydrocarbon lubricating oil antioxidant which comprises

simultaneously reacting together beta-pinene, phosphorous pentasulfide, and elemental sulfur at a temperature range of from about 115° C. to about 130° C. for a period of time not substantially exceeding four hours, the reactants being employed in the proportion of at least about 4 mols of beta-pinene and from about 0.5 to about 3 mols of sulfur for each mol of phosphorous pentasulfide.

4. A method of preparing a hydrocarbon lubricating oil antioxidant which comprises simultaneously reacting together camphene, phosphorous pentasulfide, and elemental sulfur at a temperature range of from about 115° C. to about 130° C. for a period of time not substantially exceeding four hours, the reactants being employed in the proportion of at least about 4 mols

of camphene and from about 0.5 to about 3 mols of sulfur for each mol of phosphorous pentasulfide.

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