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LUBRICANT

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This invention relates to an improved lubricant, particularly to a compounded lubricant, containing an oil-soluble derivative of a sulfur-containing acid of phosphorus characterized by the presence of at least one ester radical obtained or derived from a member of the Anacardium genus of the Anacardiaceae family.

The improved lubricants to which the present invention is directed are those lubricants which are normally subject to oxidation and corrosion conditions during service and include the petroleum lubricating oils for internal combustion engines such as Diesel oils, motor oils, heavy duty motor oils and airplane oils, together with such compounding lubricants as are used in textile oils, greases and industrial lubricants.

It has been discovered that when small amounts of an oil-soluble or oil-miscible derivative of a sulfur-containing acid of phosphorus characterized by the presence of at least one ester radical derived from an unsaturated alkyl phenol which, in turn, is derived from a member of the Anacardium genus of the Anacardiaceae family are incorporated in a hydrocarbon lubricating oil, the resulting oil, together with lubricants compounded therewith, are rendered substantially resistant to oxidation and corrosion during service.

In defining the additive ingredients of the present invention, the term "sulfur-containing acid of phophorus" is used to denote those phosphorus acids in which at least one oxygen atom has been replaced by sulfur. The arrangement of the sulfur, oxygen and phosphorus atoms within the molecule have not been definitely ascertained and in the majority of instances, the final composition comprising the additive ingredient contains a mixture of various sulfur-containing phosphorus acid radicals which contain different molecular arrangements of the sulfur, oxygen and phosphorus atoms. These phosphorus acid radicals and the esters thereof may be obtained by various methods and the structure thereof will depend upon the conditions of reaction and the particular reactants used.

The preferred type of phosphorus acid radicals are those radicals which result from the reaction of a sulfide of phosphorus, with a phenol or a metal phenolate. Other phosphorus acid radicals within the contemplation of the present invention include those resulting from the reactions of a thiophenol or thiophenolate with a phosphorus oxide, a thiophenol or thiophenolate with a sulfide of phosphorus, a thiophenol or thiophenolate with a phosphorus chloride and a phenol, thiophenol or their corresponding phenolates with a phosphorus sulfochloride. These reactions all yield a sulfur-containing phosphorus acid radical which may be either a derivative of phosphoric acid or phosphorus acid

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depending upon the valence of the phosphorus in the phosphorus sulfide, oxide, chloride or sulfochloride. Throughout the following description of the invention, phosphorus pentasulfide and the resulting thiophosphates formed from the reaction therewith will be used as illustrative of the foregoing phosphorus reactions and the resulting sulfur-containing acids of phosphorus.

The oil-soluble or oil-miscible derivatives of the sulfur-containing acids of phosphorus include the esters and metal salts of such acids which contain at least one ester radical. These ester radicals are derived from the unsaturated alkyl phenols which are present in or derived from the naturally occurring oils of the Anacardium genus of the Anacardiaceae family. Embraced within this category are the unsaturated alkyl phenols obtained or derived from such oils as cashew nut shell oil, marking nut shell oil, Japanese lac, etc., and including such specific compounds as cardanol ($C_{20}H_{32}O$), anacardol ($C_{18}H_{30}O$) and urushiol ($C_{20}H_{30}O_2$). All of the unsaturated alkyl phenols obtained or derived from these naturally occurring oils are phenols possessing one or more hydroxyl groups and substituted in the nucleus by one or more high molecular weight unsaturated alkyl radicals. In the majority of instances the alkyl radicals possess a high degree of unsaturation indicating more than one double bond which probably accounts for the instability of these compounds and their susceptibility to polymerization and condensation reactions which are characteristic of these phenols.

Of the many unsaturated alkyl phenols within the purview of the present invention, cardanol is typical and as such will be used in the following description and examples. Cardanol is not present in the naturally occurring cashew nut shell oil but is derived therefrom by the decomposition of other aromatic compounds in the oil. It is an oil-soluble phenol containing one hydroxyl group and possessing an unsaturated alkyl radical of 14 carbon atoms in the meta position. This compound may be prepared from cashew nut shell oil by any of the following methods: (1) distillation of the commercial cashew nut shell oil at greatly reduced pressure; (2) steam distillation of the commercial cashew nut shell oil at atmospheric or reduced pressure; (3) destructive distillation of the solvent extracted cashew nut shell oil; or (4) decarboxylation of the solvent extracted cashew nut shell oil with subsequent distillation or solvent extraction.

The metal salts of the invention may consist of any of the metals found in groups I, II, III, IV, VI, VII and VIII of the periodic table of elements and includes such metals as sodium, potassium, lithium, calcium, barium, strontium, tin, bismuth, aluminum, zinc, magnesium, cadmium, lead, titanium, antimony, chromium, manganese, cobalt, nickel, iron and copper with preference given to the alkaline earth metals and tin and zinc.

In compounding the additive ingredient in a hydrocarbon lubricating oil, the amount of additive incorporated in the oil is dependent upon the type of lubricant and the degree of improvement desired. In the majority of instances, the proportion of additive compounded with the oil will not exceed 5% and will vary from 0.01–5.0%. The preferred range of proportions in a mineral lubricating oil when used in a few of the more common services are as follows:

	Per cent by weight of finished lubricant
Diesel lubricating oil	0.5 –2.0
Motor lubricating oil	0.3 –1.5
Heavy duty lubricating oil	0.5 –2.5
Turbine lubricating oil	0.01–0.5
Airplane lubricating oil	0.2 –1.0

The course of reaction in preparing the additive ingredients will vary in accordance with the particular oil-soluble derivative desired. If the ester of the sulfur-containing acid of phosphorus is to be prepared, cardanol is reacted with phosphorus pentasulfide in the particular molal quantities necessary to yield either an acidic or neutral reaction product. Both the acidic and neutral reaction products have been found suitable for the purposes of the invention. If the oil-soluble derivative is to be the metal salt of the esterified sulfur-containing acid of phosporous, the reaction may proceed either directly through the reaction of the metal cardanate and phosphorus pentasulfide or indirectly through the preparation of an acidic reaction product of cardanol and phosphorus pentasulfide with subsequent neutralization to form the metal salt thereof. In all of the reactions in which cardanol or the metal cardanate is reacted with phosphorus pentasulfide, particular care is to be taken to avoid the polymerization of the cardanol molecule. This may be overcome by stepwise reactions in the presence of a hydrocarbon solvent in which small increments of the total phosphorus pentasulfide are separately reacted with the cardanol or metal cardanate. The following examples are presented as illustrating some of the foregoing methods of preparing the oil-soluble derivatives:

EXAMPLE I

700 grams of cardanol were dissolved in 700 ccs. of benzene and 228.5 grams of barium hydroxide added thereto. The reaction mixture was refluxed overnight under an automatic water separator. Upon completion of the reaction, the mass was cooled and 72 grams of phosphorus pentasulfide added. This reaction mixture was then refluxed with vigorous agitation for five hours after which it was filtered and stripped of the solvent.

1,365.5 grams of the reaction product were then retreated by dissolving in 1570 ccs. of toluene and adding thereto 78.4 grams of phosphorus pentasulfide. This mixture was then heated for four hours on the steam bath, filtered and stripped of solvent. It was found in the original reaction that refluxing in a benzene solution did not afford a high enough temperature for the reaction and, therefore, the product was retreated in a toluene solution. It was found, further, that excessive amounts of phosphorus pentasulfide tended to polymerize the cardanol and that only through stepwise treatment would the reaction proceed. The final product analyzed as follows:

	Per cent
Barium	17.4–17.6
Phosphorus	4.0
Sulfur	13.6

EXAMPLE II

125 grams of stabilized cardanol, bromine number 104 (stabilized by partial hydrogenation), was dissolved in an equal volume of toluene and added to a liquid ammonia solution of 41 grams of anhydrous stannous chloride. The reaction mixture was stirred for six hours and the ammonia allowed to evaporate overnight. Additional toluene was added and the product filtered. The toluene solution of the product was then reacted with 25 grams of phosphorus pentasulfide and heated for four hours on the steam bath. Additional toluene was then added and the mixture filtered. 20 grams of unreacted phosphorus pentasulfide were recovered and the filtrate was returned to the reaction flask and retreated with another 20 grams of phosphorus pentasulfide all of which reacted. The product was then filtered, washed and stripped of solvent. The final product analyzed as follows:

	Per cent
Tin	8.0–7.8
Phosphorus	2.8
Sulfur	7.4

EXAMPLE III

125 grams of stabilized cardanol (stabilized by partial hydrogenation), 30 grams of phosphorus pentasulfide, 155 grams of 300 pale oil and 300 ccs. of toluene were placed in a reaction flask and stirred on the steam bath for 14 hours. The reaction mixture was then filtered and stripped of solvent and the final product analyzed as follows:

	Per cent
Sulfur	11.8
Phosphorus	4.4

The effectiveness of the compositions of the present invention when incorporated in a hydrocarbon lubricating oil has been demonstrated by empirical tests designed to simulate actual operating conditions together with further tests in actual automotive engines. The following empirical test was designed to illustrate the antioxidant and/or anti-corrosive properties of the additive ingredients when incorporated in a mineral lubricating oil designed for service in internal combustion engines. This test is conducted in an apparatus consisting of a copper-lead bearing specimen encased in a special non-wearing bushing, rotatably mounted on a stainless steel shaft, and immersed in a glass pot of the oil to be tested. The oil was heated to a controlled temperature of 350° F. and continuously circulated between the bearing specimen and the shaft for a period of 10 hours. Throughout the test the oil was continuously maintained in a turbulent flow by copper baffles which acted as oxidation accelerators. The bearing specimen was weighed before the test and after the 10-hour period and the loss of weight recorded in milligrams. The reference oil used in this test was a solvent-refined, dewaxed, Mid-Continent lubricating oil of an S. A. E. 30 grade. The results of the reference oil were then used as a comparison against the reference oil compounded with the compositions prepared in the foregoing examples. For simplicity, the composition prepared in Example I which may be described as a barium salt of cardanyl thiophosphate will be referred to as sample 1; the composition prepared in Example II which may be described as a tin salt of cardanyl thiophosphate will be referred to as sample 2; and the composition prepared in Example III which may be described as a cardanyl ester of a thiophosphoric acid will be referred to as sample 3.

BEARING CORROSION—COPPER-LEAD (10 HOURS)

Loss of weight—mgs.

	350° F.
Reference oil	250
Reference oil+1.0% sample 1	0–0
Reference oil+2 0% sample 1	6–4
Reference oil+1.0% sample 2	4–2
Reference oil+0.5% sample 2	8–11
Reference oil+0.5% sample 3	6–2

The test in an automotive engine was run in a standard Chevrolet engine operated on a block for 40 hours at 2500 R. P. M. and 50 M. P. H. or an equivalent of 2000 miles with a crankcase oil temperature of 275° F. and jacket temperature of 212° F. with a crankcase ventilation of one cubic foot of air per minute. The test was stopped at a 10-hour period and started immediately. At 20 hours, the engine was stopped and rested for four hours. At 30 hours, the engine was again stopped and rested for four hours. At 40 hours, the test was terminated, the engine was taken down, the pistons removed and the amount of varnish deposit on the oil rings and piston skirt determined. This was accomplished in each case by washing first with precipitation naphtha to remove the retained oil, then washing with acetone to remove the varnish deposit. The acetone solution was then evaporated to dryness and the residue extracted with precipitation naphtha to remove the remaining traces of oil. The residue was again taken up in an acetone solution and filtered to remove suspended deposits and finally evaporated to dryness.

The following results were obtained on an uninhibited reference oil which was a solvent refined, dewaxed, Mid-Continent lubricating oil of an S. A. E. 20 grade, together with said oil, containing the additive ingredients as prepared in the foregoing examples. The designation of the compositions will follow the nomenclature given in the foregoing test. In each instance the composition to be tested was bracketed by runs on the reference oil:

	Visual piston varnish	Piston skirt varnish, mgs.	Ring varnish, mgs.	Under piston deposit, mgs.
Reference oil	Medium+	732	726	5,840
Reference oil + 2.0% sample 1.	Clean+	72	37	376
Reference oil	Heavy	675	766	7,994
Reference oil	Medium	774	633	3,653
Reference oil + 0.5% sample 2.	Clean+	45	39	3,679
Reference oil	Medium	681	394	1,023
Reference oil	do	634	554	4,571
Reference oil + 0.5% sample 3.	Clean+	95	99	0
Reference oil	Medium	302	315	942

The hydrocarbon oils to which the oil-soluble metal derivatives of the present invention are added may be either in the crude form or partially or highly refined and may contain other additive ingredients such as dyes, metal soaps, pour depressants, thickeners, V. I. improvers, oiliness agents, extreme pressure agents, sludge dispersers, oxidation inhibitors, and corrosion inhibitors, such as sulfurized hydrocarbons, etc.

Obviously many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-soluble metal salt of a sulfur-containing acid of phosphorus possessing at least one ester radical derived from an unsaturated alkyl phenol, said unsaturated alkyl phenol being derived from a member of the Anacardium genus of the Anacardiaceae family.

2. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-soluble metal salt of the reaction product of an oil-soluble phenolic composition derived from a member of the Anacardium genus of the Anacardiaceae family with a sulfide of phosphorus.

3. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-soluble reaction product of a metal salt of an oil-soluble phenolic composition derived from a member of the Anacardium genus of the Anacardiaceae family with a sulfide of phosphorus.

4. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-soluble derivative of a sulfur-containing acid of phosphorus characterized by the presence of at least one ester radical derived from a partially hydrogenated phenolic composition obtained from a member of the Anacardium genus of the Anacardiaceae family.

5. A lubricant comprising a hydrocarbon lubricating oil and 0.01–5.0% by weight of an oil-soluble metal salt of a reaction product of cardanol and a sulfide of phosphorus.

6. A lubricant comprising a hydrocarbon lubricating oil and 0.01–5.0% by weight of an oil-soluble reaction product of a metal salt of cardanol and a sulfide of phosphorus.

7. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-soluble derivative of a sulfur-containing acid of phosphorus characterized by the presence of at least one ester radical derived from a partially hydrogenated phenolic distillate of cashew nut shell oil.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,389,527	McCleary	Nov. 20, 1945
2,388,074	Patterson et al.	Oct. 30, 1945
2,361,051	Patterson et al.	Oct. 24, 1944
2,261,047	Asseff	Oct. 28, 1941
2,252,984	Rutherford	Aug. 19, 1941
2,242,260	Prutton	May 20, 1941
2,157,126	Harvey	Oct. 23, 1934