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LUBRICANTS

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This invention relates to an improved lubricant, and particularly to a compounded lubricant containing an oil-soluble metal derivative of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized alkyl phenol.

The improved lubricants to which the present invention is directed are those lubricants which are normally subject to oxidation and corrosion tendencies during service and include the petroleum lubricating oils for internal combustion engines such as Diesel oils, motor oils, heavy duty oils and aviation oils, together with the compounding lubricants such 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 metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized alkyl phenol are incorporated in a hydrocarbon lubricating oil, the resulting oil, together with lubricants compounded therewith, are rendered substantially resistant to oxidation and corrosion under operating conditions.

Although the principal function of this type of additive ingredient in a lubricating oil is the inhibition of oxidation and corrosion, other advantageous features result which enhance their value as improving agents. It has been found that besides the foregoing properties mentioned these additives increase the load-carrying or extreme pressure qualities of the oil and act as a dispersing agent for undissolved carbonaceous materials.

In defining the additive ingredients of the present invention, the term "sulfur-containing substituted acid of phosphorus" is used to denote the acidic radical or radicals obtained by reacting a sulfide of phosphorus with a phenol or metal phenolate. The arrangement of the sulfur, oxygen, and phosphorus atoms in the radicals apparently depends upon the conditions of reaction and probably results in a mixture of different types of sulfur-containing acids of phosphorus in the final composition. The particular sulfide of phosphorus used in the preparation of the additive composition depends upon whether a thio derivative of phosphoric or phosphorous acid is preferred. In the present instance the thio-derivatives of phosphoric acid are preferred and for that reason phosphorus pentasulfide will be used in the description of the invention. This is not to be construed as limiting the invention to the use of phosphorus pentasulfide or the thiophosphoric acids resulting therefrom but merely as an example of a sulfide of phosphorus and one method of preparing the sulfur-containing acids of phosphorus.

The ester substituent of the additive composition is derived from a sulfurized alkyl phenol and is linked to the sulfur-containing acid of phosphorus through the hydroxyl group. These sulfurized alkyl phenols are obtained by the sulfurization of unsaturated alkyl phenols containing one or more double bonds in the alkyl radical. The unsaturated alkyl phenol may be either a mono- or polyhydric phenol and may contain one or more unsaturated alkyl substituents attached to the nucleus. Included within this category are the unsaturated alkyl phenols which contain further substituents attached to the nucleus in the form of aliphatic or aromatic substituents. It has been found desirable to start the chain of reactions with an unsaturated alkyl phenol which is oil-soluble since the ester substituent is usually the determining factor in the oil-solubility of the final composition. The oil-solubility depends on the number of aliphatic carbon atoms attached to the nucleus of the phenols and for the purposes of the present invention the aliphatic carbon atoms should exceed five in number.

In the preferred form of the invention, the unsaturated alkyl phenols are selected from the phenolic compositions obtained or derived from the Anacardium genus of the Anacardiaceae family which includes such unsaturated alkyl phenols as cardanol ($C_{20}H_{32}O$), anacardol ($C_{18}H_{30}O$) and urushiol ($C_{20}H_{30}O_2$). These phenolic compositions are usually mono- or dihydric phenols containing long-chain unsaturated alkyl radicals attached to the nucleus and are either present in the oils such as cashew nut shell oil, marking nut shell oil, Japanese lac, etc., or are formed by the decomposition of other aromatic compounds contained therein.

The invention is not restricted to this source of unsaturated alkyl phenols and includes such unsaturated compounds as may be prepared by chlorination of high molecular weight hydrocarbons followed by condensation with a phenol and subsequent dehydrohalogenation of the chlorine atoms remaining in the alkyl radical or by chlorination of a poly substituted alkyl phenol followed by dehydrohalogenation.

These methods of preparing the unsaturated alkyl phenols are only an illustration of the various methods of preparation and may be modified or changed in accordance with the desired product.

When sulfurizing the unsaturated alkyl radicals, it is preferable to sulfurize with elemental

sulfur at comparatively low temperatures, e. g., below 200° C. in the presence of a hydrocarbon solvent. It has been found that reactions carried out at higher temperatures tend to promote polymerization of the phenol and result in oil-insoluble sulfurized products. Another suitable method for preventing polymerization in the highly unsaturated phenols is to partially hydrogenate the unsaturated alkyl radical and thereby stabilize the more reactive double bonds.

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 period table of elements and includes such metals as sodium, potassium, lithium, calcium, barium, strontium, tin, bismuth, aluminum, zinc, magnesium, cadmium, lead, titanium, antimony, chrominum, manganese, cobalt, nickel, iron and copper with preference given to the alkaline earth metals and tin and zinc.

These metal salts are formed by the neutralization of one or more acidic radicals remaining in the sulfur-containing acid of phosphorus after esterification with the sulfurized alkyl phenol. Alternatively, the esterification and neutralization steps may be combined by the reaction of the desired metal phenolate with the sulfide of phosphorus.

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%. 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 following example illustrates one of the various methods of preparing the metal salts of sulfur-containing substituted acids of phosphorus possessing at least one ester radical derived from a sulfurized alkyl phenol:

Example I

To 285 grams of partially hydrogenated cardanol (bromine number 64–65) were added 315 grams of 300 pale oil and 28 grams of elemental sulfur. The mass was heated to 150–160° C. and the sulfurization reaction was conducted for six hours. To 314 grams of the sulfurized cardanol were added 50 grams of barium hydroxide and 300 cc. of toluene. The mixture was heated on a pressure steam bath and refluxed until no more water was removed after which the product was filtered.

To the resulting barium salt of sulfurized cardanol was added 45 grams of phosphorus pentasulfide and the reaction mixture heated on the steam bath for 12 hours. This product was then cooled, filtered and stripped of the solvent. The resulting reaction product analyzed as follows:

	Per cent
Barium	7.8
Phosphorus	2.5
Sulfur	10.0

The effectiveness of the compositions of the present invention, when incorporated in a hydrocarbon lubricating oil, has been demonstrated by empirical tests which were designed to simulate actual operating conditions in automotive engines. The following empirical test was designed to illustrate the anti-oxidant 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 consists 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 agitated 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 composition prepared in the foregoing example. For simplicity, the composition prepared in the example will be referred to as barium sulfurized cardanyl thio-phosphate.

BEARING CORROSION—COPPER-LEAD (10 HOURS)

Loss of weight—mgs.

	350° F.
Reference oil	162–139
Reference oil+1.0% of barium sulfurized cardanyl thiophosphate	4–3

An additional test was carried out on a conventional Almen testing machine to demonstrate the improvement in load-carrying or extreme pressure properties produced by the incorporation of the aforementioned additive ingredients. The same reference oil and compounded oil which was used for the bearing corrosion test was used in the present Almen test. The results obtained are as follows:

ALMEN TEST

	Load in lbs.
Reference oil	5.3
Reference oil+1.0% of barium sulfurized cardanyl thiophosphate	21.6+

The hydrocarbon oils to which the additive ingredients 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.

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 lubricating oil having incorporated therein 0.01–5.0% by weight of an oil-miscible metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized unsaturated alkyl phenol containing at

least five carbon atoms in the unsaturated alkyl radical thereof.

2. A lubricant comprising a hydrocarbon lubricating oil having incorporated therein 0.01–5.0% by weight of an oil-miscible metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized phenolic composition obtained from the Anacardium genus of the Anacardiaceae family.

3. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-miscible alkaline earth metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized phenolic composition obtained from the Anacardium genus of the Anacardiaceae family.

4. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-miscible tin salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

5. A lubricant comprising a hydrocarbon oil and 0.01–5.0% by weight of an oil-miscible tin salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized phenolic composition obtained from the Anacardium genus of the Anacardiaceae family.

6. A lubricant comprising a hydrocarbon oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon oil, of an oil-miscible metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

7. A lubricant comprising a mineral lubricating oil and an amount, sufficient to impart anti-oxidant properties to said mineral lubricating oil, of an oil-miscible metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

8. A lubricant comprising a hydrocarbon oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon oil, of an oil-miscible metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized phenolic composition obtained from the Anacardium genus of the Anacardiaceae family.

9. A lubricant comprising a mineral lubricating oil and an amount, sufficient to impart anti-oxidant properties to said mineral lubricating oil, of an oil-miscible metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized phenolic composition obtained from the Anacardium genus of the Anacardiaceae family.

10. A lubricant comprising a hydrocarbon lubricating oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon lubricating oil, of an oil-soluble metal salt of the acidic reaction product obtained by reacting a sulfide of phosphorus with a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

11. A lubricant comprising a hydrocarbon lubricating oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon lubricating oil, of an oil-soluble metal salt of the acidic reaction product obtained by reacting a sulfide of phosphorus with a sulfurized phenolic composition derived from the Anacardium genus of the Anacardiaceae family.

12. A lubricant comprising a hydrocarbon lubricating oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon lubricating oil, of an oil-soluble reaction product obtained by reacting a sulfide of phosphorus with a metal salt of a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

13. A lubricant comprising a hydrocarbon oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon oil, of an oil-soluble metal salt of a sulfur-containing substituted phosphoric acid possessing at least one ester radical derived from a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

14. A lubricant comprising a hydrocarbon oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon oil, of an oil-soluble metal salt of the acidic reaction product obtained by reacting phosphorus pentasulfide with a sulfurized unsaturated alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

15. A lubricant comprising a hydrocarbon oil and an amount, sufficient to impart anti-oxidant properties to said hydrocarbon oil, of an oil-miscible alkaline earth metal salt of a sulfur-containing substituted acid of phosphorus possessing at least one ester radical derived from a sulfurized alkyl phenol containing at least five carbon atoms in the unsaturated alkyl radical thereof.

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