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OXIDATION-INHIBITED MINERAL OIL COMPOSITIONS

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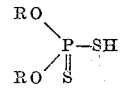
9 Claims. (Cl. 252—46.7)

The present invention relates to novel oil compositions and, particularly, to lubricating oil compositions having improved performance characteristics with respect to resistance to oxidation and corrosion of metals in contact therewith.

As is known to those skilled in the art, considerable use is made in the lubricating field of additives for lubricant compositions to impart certain desired properties to the lubricants. For example, certain mineral oil fractions, otherwise useful for lubrication purposes, have a tendency to oxidize in usage with formation of sludge or acidic products, the formation of which tends to undesirably promote corrosion of metal surfaces in contact therewith. As illustrated by the use of such mineral oil fractions for lubrication of internal combustion engines, formation of sludge or acidic products enhances corrosion of bearing surfaces, especially bearing alloys of the type now in use, that are in contact with the lubricant. Such a tendency to oxidize with formation of corrosion-promoting products is present in many mineral oil fractions, including certain refined and unrefined oils, but the tendency to oxidize is particularly apparent in mineral oil fractions that have been highly refined to produce lubricating oils meeting current requirements, particularly with respect to possessing a high viscosity index and low sludging characteristics. To produce such highly refined oils, suitable refining treatments are known to the art, and inclusive of which are conventional solvent extraction processes wherein use is made of solvents such as furfural, phenol, beta-beta-dichloroethyl ether, and others that preferentially extract the more aromatic-containing molecules from the oil. Although such treatments generally improve the oils with respect to viscosity index and other properties, they tend to decrease the resistance of the oils against oxidation, probably due to removal by such treatments of naturally contained inhibitors in the oils. Thus, to improve the oxidation and corrosion characteristics of mineral oil fractions including highly refined oils as well as certain unrefined oils that have a tendency to oxidize, and particularly those intended for use as lubricants, an additive or additives are incorporated in the oils to improve the performance characteristics of the oil composition in a particular property or combination of properties. An object of the present invention is to provide novel mineral oil compostions containing an additive material that markedly inhibits the tendency of the oil to oxidize.

The compositions embodied herein comprise a mineral oil fraction in major amount based upon the weight of the composition and a small amount, sufficient to substantially inhibit the composition against oxidation, of an oil-soluble phosphorus-, nitrogen-, and sulfur-containing material as described hereinafter. With reference to the mineral oil component, usage is contemplated of mineral oil fractions of refined or unrefined types that may vary over a rather wide range with respect to viscosity, viscosity index and other characteristics and to which fractions it is desired to impart improved anti-oxidant properties. An illustrative embodiment relates to use, as the mineral oil component, of a mineral oil fraction of lubricating grade such as heavy and light viscosity oils useful for lubrication of internal combustion engines, and the like. A preferred embodiment relates to use, as the mineral oil component, of a mineral oil fraction of lubricating grade that has been highly refined, as by solvent extraction, and to which it is desired to impart improved anti-oxidant properties.

The material incorporated in the compositions embodied herein as the oxidation and corrosion-inhibiting component is an oil-soluble product formed by addition reaction of an esterified dithiophosphoric acid with an amide of propenoic acid or substituted propenoic acids. The esterified dithiophosphoric acids contemplated for such use as a component of said addition product may be illustrated by the following structural formula:



wherein R is a hydrocarbon group that provides, when subjected to addition reaction with an amide as described hereinafter, an addition product that is sufficiently soluble in mineral oils in amounts that impart the desired improvement with respect to inhibiting oxidation of the mineral oil fraction. Thus, R may represent hydrocarbon groups such as aryl, aralkyl, alkaryl and alkyl groups, or the like, and mixtures thereof. Preferably, however, R represents an alkyl group, and particularly an alkyl group of a relatively high content of carbon atoms, e. g. from about four to about eighteen carbon atoms. Specific illustrations include heptyl, octyl, 2-ethylhexyl, lauryl, and the like.

As aforesaid, the other component of the addition reaction product is an amide of a propenoic acid. Of such amides, acrylamide is particularly suitable for practice of this invention and represents a preferred embodiment. However, the invention may be practiced with amides of substituted propenoic acids, inclusive of homologs of propenoic acid, and which may be illustrated by crotonic acid. Also contemplated for use are amides of other substituted propenoic acids, and illustrative of which is the amide of methacrylic acid.

Suitable reaction conditions for preparation of the addition products used herein comprise heating the reactants, in mol to mol ratio, at an elevated temperature, e. g. about 65° C. or higher, for about one to two hours, and allowing the thus heated product to stand at room temperature, as for example, for about one to two days.

In this manner, addition products may be prepared by reacting amides, such as acrylamide, crotonamide, and the like with esterified dithiophosphoric acids such as 0,0-di-2-ethylhexyldithiophosphoric acid, 0,0-dioctyldithiophosphoric acid, 0,0-dilauryl dithiophosphoric acid, and the like. For purposes of illustration, and without intent of limitation, the invention is described hereinafter with reference to use of an addition product prepared by the aforesaid method, using acrylamide and 0,0-di-2-ethylthexyldithiophosphoric acid, and which is a viscous red-yellow liquid readily soluble in a furfural refined mineral oil fraction of SAE 30 grade, and an addition product formed by 0,0-di-2-ethylhexyldithiophosphoric acid with crotonamide.

Compositions were prepared comprising (A) 0.5% by weight of the acrylamide addition product dissolved in a furfural refined SAE 30 oil of lubricating grade, and (B) 3% by weight of the crotonamide addition product in the same SAE oil. These compositions were subjected to the following oxygen absorption test which affords a ready method for evaluating oil compositions for oxidation and corrosion characteristics.

250 grams of the oil composition, 74–75 sq. in. of iron wire, 10 sq. in. of copper wire, and 20 sq. in. of lead foil surface are placed in a container having an inlet for oxygen and an exit tube for oxidation products and unused oxygen, the aforesaid metals being maintained immersed in the oil. Oxygen is bubbled through the oil (maintained at 150° C. and at atmospheric pressure) at the rate of 30.35 liters per hour and at the end of 20 hours the lead foil surface is cleaned and weighed and the difference between its weight before the test and the loss of weight that occurred during the test is an indication of the corrosive tendency of the oil compositions whereas the difference between the amount of oxygen bubbled through the oil and the amount of unused oxygen is indicative of the oxidation characteristics of the composition.

The following tabulation sets forth data obtained pertaining to lead loss and oxygen absorption characteristics of the aforesaid additive-containing compositions under the conditions of the test procedure and, for purposes of comparison, the tabulation sets forth corresponding lead loss and oxygen adsorption values characteristic of a furfural refined SAE 30 oil not containing the additive component of this invention.

	Comp. A	Comp. B	Furfural Refined SAE 30 Oil
Lead loss in milligrams	276	348	1,242
Oxygen Absorption (ml. O_2/hr.)	34	98	436

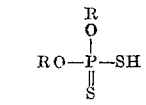
As is apparent from the data set forth hereinbefore, the phosphorus-, nitrogen-, and sulfur-containing additives embodied for use in practice of this invention function to markedly inhibit mineral oil compositions with respect to oxidation and metal corrosion characteristics.

Although, in the aforegoing illustrative example, specific concentrations of 0.5% and 3% of the additives were used in the oil compositions set forth, it should be understood that use of such concentrations is an illustrative, and not limitative, embodiment of the invention. The invention embodies use of the additive in concentrations other than specifically set forth depending on factors such as the amount required to obtain desired results in combination with a particular base oil, solubility characteristics of the particular additive employed, and the like. For most purposes, however, amounts of from about 0.02 to about 10 per cent of the additive may suitably be used based upon the weight of the composition.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will readily recognize that variations and modifications can be made. Such modifications and variations are to be considered to be within the purview of the specification and scope of the appended claims. Moreover, it should be understood that compositions, as embodied herein, may also contain additional ingredients for imparting other desired properties to the compositions. In illustration, the compositions may contain anti-foam agents, e. g. of the silicone type, viscosity index improvers, e. g. polyacrylates, and the like.

We claim:

1. A composition comprising a mineral oil in major amount based on the weight of the composition and a small amount, sufficient to substantially inhibit said composition against oxidation, of an oil-soluble addition product of a compound of the formula



wherein R represents a hydrocarbon group and an amide of an acid from the group consisting of propenoic acid and a methyl substituted propenoic acid.

2. A composition, as defined in claim 1, wherein the mineral oil is a mineral oil fraction of lubricating grade.

3. A composition, as defined in claim 2, wherein the mineral oil is a solvent refined oil.

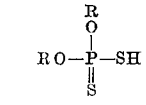
4. A composition, as defined in claim 1, wherein R represents an alkyl group.

5. A composition, as defined in claim 4, wherein R is 2-ethylhexyl.

6. A composition, as defined in claim 1, wherein the amide is acrylamide.

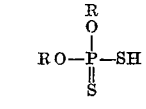
7. A composition comprising a highly refined mineral oil of lubricating grade and a small amount, sufficient to substantially inhibit the composition against oxidation, of an oil-soluble addition product of 0,0-di-2-ethylhexyldithiophosphoric acid and an amide from the group consisting of acrylamide and crotonamide.

8. A composition comprising a mineral oil of lubricating grade in major amount based on the weight of the composition and a small amount, sufficient to inhibit said composition against oxidation, of an oil-soluble addition product of a compound of the following formula:



wherein R is an alkyl group of from about four to about eighteen carbon atoms and an amide of an acid from the group consisting of propenoic acid and methyl-substituted propenoic acid.

9. A composition comprising a mineral oil in major amount based on the weight of the composition and a small amount, sufficient to inhibit said composition against oxidation, of an oil-soluble oxidation-inhibiting addition product of a compound of the formula



wherein R represents a hydrocarbon group and an amide of an acid from the group consisting of propenoic acid and an alkyl-substituted propenoic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,566,129	Hook et al.	Aug. 28, 1951
2,630,451	Fletcher et al.	Mar. 3, 1953
2,682,508	Godfrey	June 29, 1954