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LUBRICATING COMPOSITION

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The present invention relates to improved lubricants and particularly to a lubricating composition containing one or more additive ingredients capable of imparting detergent and anticorrosive properties thereto.

The additive ingredients of the present invention are prepared from the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family. The oils included within this classification are the oils and liquids commonly referred to as cashew nut shell oil, marking nut shell oil, Japanese lac, etc., whose chemical composition depends upon the particular method of extraction used. It is the consensus of the authorities on these extracted oils and liquids that the chemical composition of the naturally-occurring oils consists primarily of various types of aromatic derivatives, such as anacardic acid ($C_{22}H_{32}O_3$), cardol ($C_{32}H_{52}O_4$), cardanol ($C_{20}H_{32}O$), anacardol ($C_{18}H_{30}O$), urushiol ($C_{20}H_{30}O_2$), etc. These aromatic derivatives, and the other aromatic derivatives which may be present in or derived from the oils which have not been isolated, are very unstable and in the presence of heat form decomposition products or oil-insoluble polymerization products.

For the purposes of this invention, one of these naturally-occurring oils, namely, cashew nut shell oil, will be used as illustrating the types of derivatives and reactions representative of the components of the oils falling within this natural classification. Cashew nut shell oil, when obtained by solvent extraction, consists primarily of 90% anacardic acid and 10% cardol. The anacardic acid portion of this solvent-extracted oil, which is described as a salicylic acid homolog, decomposes at slightly elevated temperatures with the evolution of carbon dioxide to yield cardanol, which is a phenol containing an unsaturated alkyl radical ($C_{14}H_{27}$) in the meta position. This decomposition is particularly noticed in the cashew nut shell oil obtained by a thermal extraction process which contains varying amounts of anacardic acid, usually around 16%, with the balance made up of a major proportion of cardanol and a minor proportion of cardol.

It has been found that certain derivatives of these phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, when incorporated in a lubricating composition, impart enhanced detergent properties thereto. The derivatives of these phenolic compositions with which the present invention is concerned are the oil-miscible aliphatic-ether-alcohol and the aliphatic-ether-alcoholate derivatives of these phenolic compositions.

In referring to the "phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family," it is to be understood that such a classification includes all those aromatic derivatives obtained from these oils which possess at least one hydroxyl group attached to the aromatic nucleus irrespective of the presence of other oxygen-containing radicals, which may also be attached to the nucleus together with mixtures thereof.

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The aliphatic-ether-alcohol derivatives of these phenolic compositions are those in which a hydroxyl or sulfhydryl radical is displaced from the aromatic nucleus of the phenolic composition by means of an aliphatic radical linked to the aromatic nucleus through an ether linkage at the position of one or more of the original hydroxyl groups. The displaced hydroxyl or sulfhydryl radical may remain as such in the final product or the replaceable hydrogen thereof may be replaced by a metal to form the metal alcoholate derivative, depending upon the type of improving qualities desired in the compounded lubricant.

The additive ingredients of the present invention may be described as those oil-miscible derivatives of the phenolic compositions present in or derived from the Anacardium genus of the Anacardiaceae family which possesses the following general formula

$$A((RX)_aY)_n$$

in which A is a phenoxy radical derived from the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, R is an aliphatic radical, X may be either oxygen or sulfur, Y may be either hydrogen or a metal, and a and n are integers of one or more. The value of n may be varied in accordance with the number of hydroxyl radicals present on the nucleus of the phenolic composition. The value of a is preferably within the range of from 1 to 10. The radical R, although referring broadly to any aliphatic radical, is preferably one containing from 1 to 10 carbon atoms which may contain such substituents as halogen, amino, nitro, sulfur, etc., radicals attached thereto. The symbol Y designates the replaceable hydrogen of the aliphatic-ether-alcohol derivative or the presence of a metal, as in the aliphatic-ether-alcoholate derivative, which metal has one valence thereof attached to the constituent X of the formula. The metals contemplated within the designation of Y may be any of the following metals, such as lithium, sodium, potassium, calcium, barium, strontium, magnesium, zinc, iron, cadmium, nickel, manganese, tin, mercury, copper, aluminum, lead, etc., with particular preference given to the alkaline earth metals.

In view of the fact that the phenoxy radical A is derived from the phenolic compositions of

the Anacardium oils which are extremely unstable and susceptible to polymerization and condensation reactions, it may be preferable to first stabilize these compositions before proceeding in the preparation of the derivatives of the present invention. Such stabilizing processes include partial hydrogenation or addition reactions which render the unsaturated alkyl constituents of these compositions less reactive and may, in effect, enhance the improving properties of the final product as an addition agent. It is therefore to be understood that the scope of the invention includes the stabilized as well as the unstabilized phenolic compositions when reference is made to these phenolic compositions or the phenoxy radical A.

Another factor to be considered in the interpretation of the scope of the invention is that when reference is made to the aliphatic-ether-alcohol and alcoholate derivatives, such nomenclature is intended to include the derivatives in which the alcohol or alcoholate portion thereof is replaced by a sulfhydryl radical or the metal salts of such compounds.

These additive components may be incorporated in a hydrocarbon oil, and preferably in a mineral lubricating oil, in amounts varying between 0.01 and 5.0% by weight, depending upon the type of base oil and the degree of improvement desired. It has been found that when using a mineral lubricating oil as the base oil in a lubricating composition designed for service in internal combustion engines the range of proportions between 0.1 and 2.0% by weight is particularly effective.

In preparing the additive components of the present invention any of the classical methods of synthesis may be used. The particular method chosen depends upon the conditions of reaction and the stability of the phenolic composition. It is preferable to select a method of preparation which is carried out at low temperatures and which either does not yield acidic by-products or in which the acidic by-products are removed from the reaction zone. These conditions of reaction, however, may be modified if the starting material has been stabilized by partial hydrogenation or addition reactions, such as a halogenation or sulfurization reaction.

For purposes of illustration a few of the generally-accepted methods of synthesis which may be used in the preparation of these derivatives will be presented by means of empirical reactions. In these reactions the symbol AH will be used to designate the phenolic composition obtained from the Anacardium oils in which A is the phenoxy radical previously described.

(1) $AH + Cl\text{-}CH_2\text{-}CH_2\text{-}OH + NaOH \longrightarrow A\text{-}CH_2\text{-}CH_2\text{-}OH$

(2) $AH + C_2H_4O + NaOH \longrightarrow A\text{—}CH_2\text{—}CH_2\text{—}OH$

(3) $AH + yC_2H_4O + NaOH \longrightarrow A\text{—}(CH_2\text{—}CH_2\text{—}O)_yH$

(4) $ANa + Cl\text{—}CH_2\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_3 \longrightarrow A\text{—}CH_2\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_3$

(5) $ANa + Cl\text{—}(CH_2)_{10}\text{—}Cl \longrightarrow A\text{—}(CH_2)_{10}\text{—}Cl$

$A\text{—}(CH_2)_{10}\text{—}Cl + NaOH \longrightarrow A\text{—}(CH_2)_{10}\text{—}OH$

(6) $AH + Cl\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3 + Na \xrightarrow[NH_3]{liq.} A\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3$

The methods of preparing the metal salts or alcoholates will vary in accordance with the particular metal alcoholate desired. The following empirical reactions will illustrate some of the methods of preparation. In these reactions the

formula AR_1OH is used to designate the aliphatic-ether-alcohol derivatives previously described:

(1) $AR_1OH + Na \xrightarrow[\text{solvent (toluene)}]{\text{inert}} AR_1ONa$

(2) $2AR_1OH + Ca \xrightarrow[NH_3]{\text{liq.}} (AR_1O)_2Ca$

(3) $3AR_1OH + Al(OC_4H_9)_3 \longrightarrow (AR_1O)_3Al$

(4) $2AR_1OH + Ba(OH)_2 \longrightarrow (AR_1O)_2Ba$

The following specific examples illustrate the foregoing methods of preparing the compounds of the present invention:

Example I

46 grams of sodium were dissolved in two liters of liquid ammonia. To this solution was then added a toluene solution of 510 grams of cardanol with vigorous agitation. The resulting solution possessed a yellow color and 15 grams of additional sodium were added. Thereafter, one liter of toluene was added to the solution of the resulting sodium cardanate, and 210 grams of ethylene chlorhydrin were added to the solution. After standing over night at room temperature to allow the ammonia to evaporate, the toluene solution was filtered and the solvent was then removed by heating in vacuo. The residue, a reddish brown oil weighing 600 grams, consisted of cardanoxyethanol.

Example II

The cardanoxyethanol, prepared in accordance with Example I, was then taken up by one liter of toluene and added to a solution of 45 grams of calcium in two liters of liquid ammonia. An additional liter of toluene was added and the ammonia allowed to evaporate. The toluene solution was then warmed and filtered. After filtering the solvent was removed by heating in vacuo and the residual calcium cardanoxyethylate was dissolved in an equal weight of 300 pale oil to form a 50% concentrate. The 50% concentrate analyzed as follows:

	Per cent
Ash	5.8
Calcium	3.2
Sodium	0.55

Example III

610 grams of cardanol (bromine No. 124; neut. No. 1.28; hydroxyl No. 188; per cent sulfur 0.02) were dissolved in 500 ccs. of formula 30 alcohol and 120 grams of sodium hydroxide and 500 ccs. of water were added. The reaction mixture was heated at 75–80° C. with vigorous stirring to insure complete solution of the sodium hydroxide. Thereafter 260 grams of ethylene chlorhydrin were added dropwise to the mixture over a period of one hour. The agitation was continued at 75–80° C. for two hours. Some toluene was added and the oil-layer washed three times in water. 850 grams of an S. A. E.-10 grade lubricating oil and 236 grams of anhydrous barium hydroxide were added to the washed cardanoxyethanol and the mixture heated under a reflux condenser equipped with an automatic separator until all the water and toluene were removed. The maximum reaction temperature was 225° C. The resulting product was filtered while still hot. The resulting 50% concentrate of barium cardanoxyethanol in a lubricating oil analyzed 8.88% barium.

An additional feature of the present invention

is the combination of the foregoing additive component with an additive ingredient possessing anti-corrosive properties when used in lubricating compositions designed for service in which bearing corrosion is an important factor. Thus, the combination of an aliphatic-ether-alcohol or alcoholate derivative of the phenolic compositions of the Anacardium oils with an additive ingredient possessing anti-corrosive properties provides an additive combination which when incorporated in a hydrocarbon oil, and particularly a mineral lubricating oil, imparts exceptional detergent and anti-corrosive properties thereto. The class of compounds which may be used as the additive ingredient possessing anti-corrosive properties may be any one of the generally-accepted corrosion inhibitors which have been proposed and utilized by the prior art. It is preferable, however, to use an oil-soluble corrosion inhibitor which contains sulfur in the molecule in one form or another. Among the sulfur-containing anti-corrosive agents which are particularly adapted to the present invention may be mentioned the N-aliphatic thiocarbamates and the sulfur-containing kerosene fractions such as are obtained by halogenation and followed by treatment with sodium sulfide. The amounts of these additive ingredients possessing anti-corrosive properties which may be added in combination with the detergent components previously described, are usually within the proportionate range of 0.1 to 5% and preferably between the range of 0.2 to 3%, depending upon the degree of anti-corrosive properties desired.

To illustrate the effectiveness of the compounds of the present invention, together with combinations thereof with additive ingredients possessing anti-corrosive properties, the following test results are presented. A corrosion test designed to predict the corrosion inhibiting properties of compounded oils with respect to the corrosion of copper-lead bearings was used. This test consists of a copper-lead bearing specimen encased in a special non-wear bushing, rotatably mounted on a stainless steel shaft and immersed in a glass pot of the oil to be tested. The tested oil was heated to a controlled temperature of 350° F. and continuously circulated between the bearing specimen and the shaft for ten hours. Throughout the test the oil was continuously agitated by means of copper baffles which acted as oxidation accelerators. The bearing specimen was weighed before the test and after the ten-hour period and the loss in weight recorded in milligrams. The reference oil of this test was a mixed base solvent-refined, dewaxed, Mid-Continent lubricating oil of an S. A. E. 30 grade. To the reference oil was added varying proportions of the additives of the present invention taken individually and in combination and the results compared. The results of two runs at 350° F. are presented:

Bearing corrosion—copper lead (10 hours)

[Loss of weight in Mg.]

Oil tested	350° F
Reference oil	250, 300
Reference oil+0.75% calcium cardanoxyethylate	291, 155
Reference oil+0.75% calcium cardanoxyethylate+1.0% sulfur-containing kerosene fraction	4, 2
Reference oil+1.0% barium cardanoxyethylate	205, 156
Reference oil+1.0% barium cardanoxyethylate+0.5% zinc dibutyl dithiocarbamate+0.25 sulfur-containing kerosene fraction	2, 2

A further test designed to indicate the effectiveness of compounded oils under actual operating conditions was conducted. This test is a modification of the test described in Diesel Lubricant Test Manual, Laboratory Test No. 1, issued by the Caterpillar Tractor Company. This test was carried out in a single cylinder Diesel engine operating at 900 R. P. M. with a water jacket temperature of 175° F. and run continuously for periods of 120, 240, 360 and 480 hours or until rings are stuck as indicated by the increase in blowby. The crankcase oil was drained every 60 hours and fresh oil added thereto. At the end of each test period the engine was thoroughly examined and any carbonaceous deposits, lacquer and sludge formation, etc., were noted and the principal engine parts classified according to their condition. In the present instance the reference oil was a mixed base solvent-refined, dewaxed Mid-Continent lubricating oil of an S. A. E. 30 grade. The results of the test runs on the reference oil and the reference oil containing 0.5% calcium cardanoxyethylate are as follows:

Engine part	Reference oil, 120 hours	Reference oil +0.5% cardanoxyethylate, 120 hours
Heat grooves	Up to 50% plugged	Up to 50% plugged.
Ring grooves	Clean to heavy lacquer	Slight carbon in No. 1 and No. 2 grooves.
Piston skirt	Heavy varnish to lacquer.	Trace varnish to light varnish.
Under piston deposit.	Trace deposit	Trace deposit.
Filter	Clean to mesh pattern visible.	Clean to mesh pattern visible.
Ring land	Heavy varnish to carbon deposit.	Clean to heavy varnish.
Rings stuck	None	None.
Ring cleanliness.	Nos. 1, 2, 3 clean, Nos. 4, 5, 6 light lacquer.	Nos. 1 and 2 clean, Nos. 3 and 6 trace lacquer, Nos. 4 and 5 light to medium lacquer.

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 lubricating composition comprising a major amount of a hydrocarbon oil and a minor proportion, sufficient to impart detergent properties to said oil, of an oil-miscible compound of the class consisting of an aliphatic-ether-alcohol and an aliphatic-ether-metal alcoholate derivative of the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family.

2. A lubricating composition comprising a major proportion of a hydrocarbon oil and 0.01–5% by weight of an oil-miscible aliphatic-ether-alcohol derivative of the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family.

3. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01–5% by weight of an oil-miscible aliphatic-ether-metal alcoholate derivative of the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family.

4. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01–5% by weight of an oil-miscible aliphatic-ether-alkaline earth metal alcoholate derivative of the phenolic compositions present in or derived from the oils

extracted from the Anacardium genus of the Anacardiaceae family.

5. A lubricating composition comprising a major amount of a hydrocarbon oil and the combination of 0.01–5.0% by weight of an oil-miscible aliphatic-ether-metal alcoholate derivative of the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, and 0.1–5.0% by weight of an oil-miscible sulfur-containing additive ingredient possessing anti-corrosive properties.

6. A lubricating composition comprising a major amount of a mineral lubricating oil and the combination of 0.01–5.0% by weight of an oil-miscible aliphatic-ether-metal alcoholate derivative of the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, and 0.1–5.0% by weight of an oil-miscible sulfur-containing additive ingredient possessing anti-corrosive properties.

7. A lubricating composition comprising a major amount of a mineral lubricating oil and the combination of 0.01–5.0% by weight of an oil-miscible aliphatic-ether-metal alcoholate derivative of the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, and 0.1–5.0% by weight of an oil-miscible N-aliphatic di-thio-carbamate.

8. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01–5.0% by weight of an oil-miscible compound of the general formula

$$A((RX)_aY)_n$$

in which A is a phenoxy radical derived from the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, R is an aliphatic radical, X is a member from the group consisting of oxygen or sulfur, Y is a member from the group consisting of hydrogen and a metal, and a and n are integers of at least one.

9. A lubricating composition comprising a major amount of a mineral lubricating oil and 0.01%–5.0% by weight of an oil-miscible compound of the general formula

$$A((RX)_aY)_n$$

in which A is a phenoxy radical derived from the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, R is an aliphatic radical, X is a member from the group consisting of oxygen or sulfur, Y is a member from the group consisting of hydrogen and a metal, and a and n are integers of at least one.

10. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01%–5.0% by weight of an oil-miscible compound of the general formula

$$A((RX)_aY)_n$$

in which A is a phenoxy radical derived from the phenolic compositions present in or derived from the oils extracted from the Anacardium genus of the Anacardiaceae family, R is an aliphatic radical, X is a member from the group consisting of oxygen or sulfur, Y is an alkaline earth metal, and a and n are integers of at least one.

11. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01%–5.0% by weight of an oil-miscible aliphatic-ether-alcohol derivative of the phenolic compositions present in or derived from cashew nut shell oil.

12. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01–5.0% by weight of an oil-miscible aliphatic-ether-metal alcoholate derivative of the phenolic compositions present in or derived from cashew nut shell oil.

13. A lubricating composition comprising a major amount of a hydrocarbon oil and 0.01–5.0% by weight of an oil-miscible aliphatic-ether-alkaline earth metal alcoholate derivative of the phenolic compositions present in or derived from cashew nut shell oil.

14. A lubricating composition comprising a major amount of a mineral lubricating oil and 0.01–5.0% by weight of an oil-miscible aliphatic-ether-metal alcoholate derivative of cardanol.

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