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LUBRICANT COMPOSITIONS

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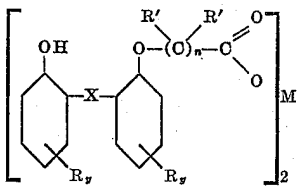
6 Claims. (Cl. 252—33.6)

This invention relates to improved lubricants for use in internal combustion engines and, in particular, to lubricating compositions having improved detergent characteristics.

In the lubrication of internal combustion engines, such as automotive and aviation engines, lubricants such as mineral lubricating oils frequently prove unsatisfactory because of their tendency to deposit varnish, gum and sludge on the metallic engine surfaces coming in contact with the lubricants. We have found that a lubricating composition having incorporated therein a relatively small amount of a metal salt represented in general by the following formula:

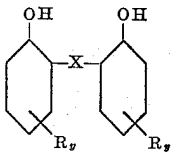


where n is an integer from 1 to 3, preferably from 2 to 3, y is an integer from 1 to 4, X is a substituent selected from the group consisting of S and

M is a divalent metal selected from the group consisting of calcium, nickel, barium, zinc and lead, R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl, and R′ is a substituent selected from the group consisting of hydrogen and alkyl; the alkyl substituent can include in its structure, among others, elements such as those of oxygen and sulfur provided they are not present in such position or in such amounts as to adversely affect the reactions incident to the formation of said metal salt, the oil solubility of the metal salt prepared therefrom, or of the lubricating composition to which they are added; and the number of carbon atoms in the alkyl, cycloalkyl, alkaryl, aryl and aralkyl groups, that is, where the substituent is R, are no more than about 32 and preferably between about 4 and about 30; substantially overcomes the accumulation of harmful engine deposits. If desired, X can be a disulfide or a polysulfide structure or it can be selenium. The aromatic nucleus shown above need not be limited to a single benzene nucleus but can be a condensed aromatic nucleus as exemplified by naphthalene, anthracene, and the like. For instance, we have found that the presence of a relatively small amount of the metal salt encompassed by the above-identified formula in a mineral lubricating oil substantially inhibits the formation of engine deposits normally encountered when using mineral lubricating oil.

The above-identified metal salts which are incorporated in the lubricating compositions in accordance with

our invention are advantageously prepared by reacting a saturated lactone and a bis-phenolic compound represented in general by the following formula:

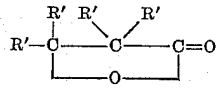


where y is an integer from 1 to 4, X is a substituent selected from the group consisting of S and

R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl, and R′ is a substituent selected from the group consisting of hydrogen and alkyl, such as methyl, ethyl, propyl, butyl, octyl or the like. The number of carbon atoms in the alkyl, cycloalkyl, alkaryl, aryl and aralkyl groups, that is, where the substituent is R, are no more than about 32 and preferably between about 4 and about 30. Higher molecular weight polyphenolic compounds of the above type containing up to about 7 nuclei bridged together by S atoms or

groups can also be employed.

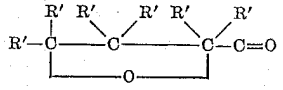
The preferred saturated lactone which is used in preparing the above-identified metal salts can be represented in general by the following formula:



where R′ is a substituent selected from the group consisting of hydrogen and alkyl, such as methyl, ethyl, propyl, butyl, octyl or the like. Thus beta-propiolactone, substituted beta-propiolactone, and homologs thereof are suitable for use in preparing the metal salts which are to be incorporated in the lubricating compositions in accordance with our invention. Specific examples of beta-propiolactones which can be used are alpha-isopropyl-beta-propiolactone, alpha - butyl - beta - propiolactone, beta-butyrolactone, alpha-ethyl-beta-butyrolactone, beta-isobutyrolactone, beta-valerolactone, beta-methyl-beta-valerolactone and beta-caprolactone.

In preparing the metal salts identified above for incorporation in lubricating compositions, we employ as the preferred bis-phenolic compounds bis(dialkylphenol) sulfides and, in particular, bis(diamylphenol) sulfide.

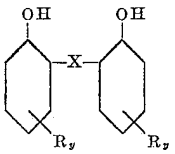
While we have stated that saturated beta-lactones are preferred for the preparation of the metal salts which are incorporated in the lubricating compositions in accordance with our invention, our invention is not so limited but may be practiced with reaction products obtained from the use of other saturated lactones. Lactones other than the saturated beta-lactones identified above which can be used include saturated gamma-lactones having the following general formula:



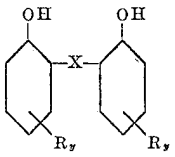
where R′ is similar in character and structure as that in the saturated beta-lactones identified above.

In preparing the desired metal salts, it is desirable to

bring the reactants into effective contact with each other to enable the reaction to proceed smoothly and economically. It is known that saturated lactones and the alkali metal salts such as the potassium, sodium and lithium salts of bis-phenolic compounds having the following general formula:



will dissolve in a polar solvent such as water or alcohol, thus permitting the contact desired to effect reaction. Accordingly, the compound having the formula:



is initially converted to the alkali metal salt such as the potassium, sodium or lithium salt; in such form is reacted with the saturated lactone in a polar solvent; and the reaction product obtained is then converted to the desired metal salt which is incorporated in the lubricating compositions in accordance with our invention. By thus bringing the reactants into effective contact with each other, no special reaction conditions are necessary to obtain the desired reaction product. The reactions proceed smoothly and efficiently at a temperature of about 20° to about 100° C. The amounts of reactants necessary to produce the desired metal salt are not critical and can be varied widely, although it is sometimes desirable that an excess of the starting bis-phenolic compound be present.

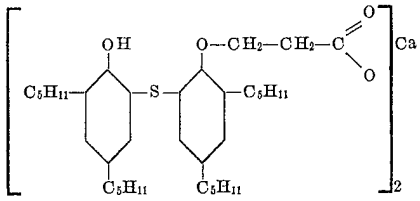
Generally, the addition of about 0.5 to about 20 percent by weight and preferably from about 1.0 to about 10 percent by weight of the metal salts, based upon the lubricant, is sufficient to effect the desired improvement in the lubricant.

The following example shows the preparation of the calcium salt of the reaction product obtained on reaction of beta-propiolactone with bis(2,4-diamylphenol) sulfide, which is representative of the metal salts which can be incorporated in lubricating oils to improve their detergency in accordance with our invention.

EXAMPLE 1

One mol of bis(2,4-diamylphenol) sulfide was stirred with one molar equivalent of sodium hydroxide in 100 milliliters of water. The temperature of the mixture increased from about 26° to about 43° C. and an emulsion formed. Acetone was added in an amount to give 1,200 milliliters of a clear dark brown solution which was cooled to 28° C. To this solution was added one molar equivalent of beta-propiolactone. The temperature of the solution increased to about 41° C. and the mixture became slightly cloudy. When the first of a solution of 110 grams of calcium chloride in water was added, the mixture separated into two layers. Addition of more acetone did not result in a single phase. However, the addition of 95 percent ethyl alcohol produced a homogeneous solution. The remaining calcium chloride solution was added with stirring, with the temperature being maintained at about 55° to 60° C. during the addition. Two layers formed on standing. The water layer was removed and then extracted with hexane. The hexane solution was added to the organic portion of the product which was thoroughly water washed. After the solvent was removed there were 587 grams of the calcium salt

of 2'-hydroxy-3',5'-diamyl-2-carboxyethoxy-3,5-diamyldiphenylthiamethane having the following structure:



The following example shows the improved detergency properties of a mineral oil lubricant having incorporated therein the calcium salt such as that prepared in Example 1.

EXAMPLE 2

A mineral oil containing 7.9 percent by weight of the calcium salt prepared in Example 1 and analyzing 0.92 ash as calcium sulfate was prepared. The oil analysis of the base oil and the blend were as follows:

	Base Oil	Blend
Gravity, °API	27.8	24.6
Viscosity, SUS:		
100° F	457	578
130° F	208	254
210° F	60.8	66.4
V. I.	95	92
Flash Point, ° F	470	360
Fire Point, ° F	545	380
Pour Point, ° F	+5	0
Color (NPA)	3—	8—
Sulfur, percent	0.22	1.05
Carbon Residue, percent	0.07	1.09
Ash ($CaSO_4$)	<0.01	0.92

The blend of mineral oil and detergent was tested in accordance with S/C Lauson (Diesel Procedure) Test and the results are tabulated below in Table I.

Table I

Hours	Piston Varnish Rating	Number of Stuck Rings
24	9+	0
48	9+	0
72	9+	0
96	9+	0
120	9+	0
144	9+	0
168	9+	0
192	9+	0
216	9+	0

The S/C Lauson (Diesel Procedure) Test employed in Table I is conducted in the following manner. A single-cylinder Lauson engine developing three horsepower is charged with 2.1 pounds of test oil and operated at full load at a speed of 1860±10 revolutions per minute with an oil temperature of 225° F.±2° F. and a coolant temperature of 300° F.±2° F. At the end of each 24 hours of operation, the engine is stopped and observations are made on the piston skirt deposit and on the piston ring condition. The piston skirt deposit is rated on a scale of 0 to 10, where 10 is a rating for a piston with no deposits and 0 for a piston with very heavy deposits. The piston ring condition is observed for tightness, sticking and/or plugging of rings. Plugging applies only to the oil rings. The test is continued for a total of 216 hours, unless excessive deposits or sticking of rings occur earlier in the test.

The results set forth in Table I show the effectiveness of the calcium salt of 2'-hydroxy-3',5'-diamyl-2-carboxyethoxy-3,5-diamyl-diphenylthiamethane as a detergent in mineral oils. At the end of the test period of 216 hours, the piston varnish rating was 9+, indicating only very slight deposits of varnish on the piston and there were no stuck rings. When the base oil alone was subjected to the S/C Lauson (Diesel Procedure) Test, after

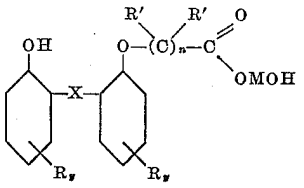
only 48 hours of operation the piston varnish rating was one, indicating very heavy deposits, and there was one stuck ring.

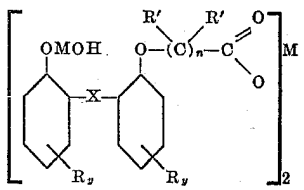
While in Example 1 we have used beta-propiolactone in the preparation of the metal salt, we can use a beta-halopropionic acid, such as beta-chloropropionic acid, in its place without affecting the composition or structure of the calcium salt. Similarly, if desired, we can employ chloroacetic acid in place of beta-chloropropionic acid in the preparation of metal salts suitable for incorporation in lubricating compositions in accordance with our invention. In such case a carboxymethoxy derivative would be obtained instead of a carboxyethoxy derivative.

In preparing the improved oil lubricants of our invention, we can also incorporate in the lubricants other addition agents normally added to lubricating oils for a specific purpose such as antioxidants, pour point depressants, corrosion inhibitors, foam suppressants, viscosity index improvers and the like, without adversely affecting the detergent benefits of this invention.

While we have shown in the examples the improved detergency properties of mineral lubricating oils having incorporated therein a relatively small amount of the above-identified metal salts, it is to be understood that improved lubricating compositions in accordance with our invention can be prepared by using other lubricating oils in place of mineral oils. Included among the lubricating oils having incorporated therein the desired metal salts which can be prepared in accordance with our invention are hydrocarbon lubricating oils, such as those produced in the Fischer-Tropsch process, and synthetic oils, such as those based on esters of dibasic acids.

While we have specifically illustrated an improved lubricant composition having incorporated therein a small amount of a neutral metal salt of the reaction product of a bis-phenol sulfide or a bis-phenol alkane with a lactone, it is to be noted that our invention is not so limited but includes improved lubricant compositions having incorporated therein small amounts of metal salts prepared from the reaction of bis-phenol sulfides or bis-phenol alkanes with lactones and metal compounds wherein the proportions of reactants are varied from those employed hereinabove. Examples of basic metal salts which can be incorporated in lubricant compositions in accordance with our invention to improve the detergency characteristics thereof can be represented in general by the following formulas:

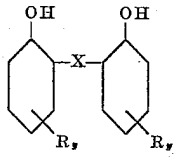




As before, in the above formulas n is an integer from 1 to 3, preferably from 2 to 3; y is an integer from 1 to 4; X is a substituent selected from the group consisting of S and

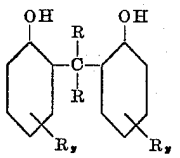
M is a divalent metal selected from the group consisting of calcium, nickel, barium, zinc and lead; R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl; and R′ is a substituent selected from the group consisting of hydrogen and alkyl.

Although we have specifically disclosed hereinabove that metal salts which can be incorporated in lubricating compositions in accordance with our invention are advantageously prepared from reaction products obtained by reacting a saturated lactone and a bis-phenolic compound represented in general by the following formula:



where y is an integer from 1 to 4, X is a substituent selected from the group consisting of sulfur and

R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl, and R′ is a substituent selected from the group consisting of hydrogen and alkyl, it is within the scope of our invention to employ a bis-phenolic compound represented in general by the following formula in the preparation of the metal salt:

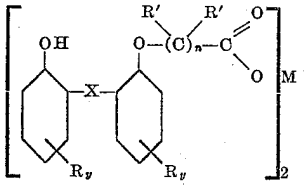


where y is an integer from 1 to 4 and R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl.

Obviously, many modifications and variations of the invention as hereinabove 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.

We claim:

1. A lubricant composition comprises a major amount of a lubricating oil and a minor amount sufficient to improve the detergency characteristics thereof of a metal salt represented in general by the following formula:

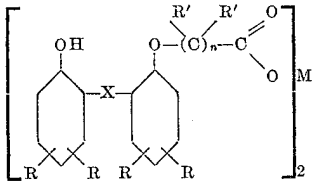


where n is an integer from 1 to 3, y is an integer from 1 to 4, X is a substituent selected from the group consisting of S and

M is a divalent metal selected from the group consisting of calcium, nickel, barium, zinc and lead, R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl, and R′ is a substituent selected from the group consisting of hydrogen and alkyl.

2. A lubricant composition comprising a major amount of a lubricating oil and a minor amount sufficient to

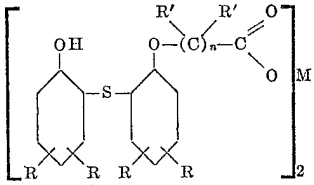
improve the detergency characteristics thereof of a metal salt represented in general by the following formula:



where n is an integer from 2 to 3, X is a substituent selected from the group consisting of S and

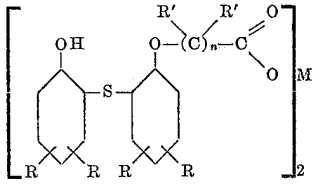
M is a divalent metal selected from the group consisting of calcium, nickel, barium, zinc and lead, R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl, and R′ is a substituent selected from the group consisting of hydrogen and alkyl.

3. A lubricant composition comprising a major amount of a lubricating oil and a minor amount sufficient to improve the detergency characteristics thereof of a metal salt represented in general by the following formula:



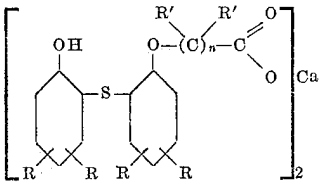
where n=2, M is a divalent metal selected from the group consisting of calcium, nickel, barium, zinc and lead, R is a substituent selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkaryl, aryl and aralkyl, and R′ is a substituent selected from the group consisting of hydrogen and alkyl.

4. A lubricant composition comprising a major amount of a lubricating oil and a minor amount sufficient to improve the detergency characteristics thereof of a metal salt represented in general by the following formula:



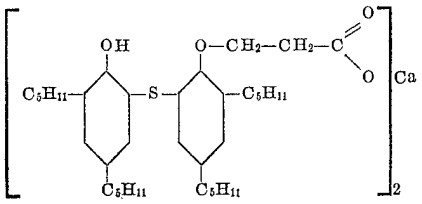
where n=2, M is a divalent metal selected from the group consisting of calcium, nickel, barium, zinc and lead, and R and R′ are substituents selected from the group consisting of hydrogen and alkyl.

5. A lubricant composition comprising a major amount of a lubricating oil and a minor amount sufficient to improve the detergency characteristics thereof of a metal salt represented in general by the following formula:



where n=2 and R and R′ are substituents selected from the group consisting of hydrogen and alkyl.

6. A lubricant composition comprising a major amount of a lubricating oil and a minor amount sufficient to improve the detergency characteristics thereof of a metal salt represented in general by the following formula:



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