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LUBRICANT COMPOSITIONS

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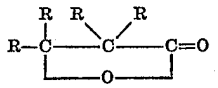
This invention relates to improved lubricants for use in internal combustion engines and in particular to lubricating compositions having improved detergent characteristics.

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 of an acyloxy carboxylic acid substantially overcomes the accumulation of harmful engine deposits. For instance, we have found that the presence of a relatively small amount of a metal salt of an acyloxy carboxylic acid in a mineral lubricating oil substantially inhibits the formation of engine deposits normally encountered when using mineral lubricating oil.

The metal salts of acyloxy carboxylic acids which are incorporated in the lubricating compositions in accordance with our invention are advantageously prepared by reacting a saturated lactone with a carboxylic acid.

The saturated lactones which are employed in preparing the metal salts of acyloxy carboxylic acids which are incorporated in the lubricating compositions in accordance with our invention are preferably those represented by the following structural formula:



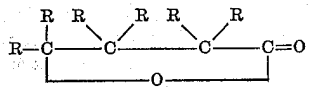
where R is a substituent selected from the group consisting of hydrogen and alkyl, such as methyl, ethyl, propyl, butyl or the like. The alkyl substituent can include in its structure, among others, elements such as those of oxygen and sulfur, provided they are not present in such position or in such amounts as to adversely affect the course of the reaction in which the saturated lactone is employed, or the oil-solubility of the metal salt prepared therefrom. 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 of acyloxy carboxylic acids, we employ naphthenic acids as the preferred carboxylic acid. While any of the available naphthenic acids can be employed in the preparation of the detergents, we prefer to employ naphthenic acids having the following properties:

Neutralization number	150 to 400
Molecular weight	200 to 400

Included among the naphthenic acids which can be employed in the reaction producing the metal salts of the acyloxy carboxylic acids are polycyclic as well as polycarboxy naphthenic acids whose metal salts are oil soluble. We have obtained especially good results with naphthenic acids recovered from petroleum oils.

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



where R is similar in character and structure as that in the saturated beta-lactones identified above. Carboxylic acids other than the naphthenic acids referred to above which can be employed include tall oil acids, phenyl-stearic acid and salicylic acid.

In preparing the desired metal salts of acyloxy carboxylic acids 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 the saturated lactones and the alkali metal salts such as the potassium, sodium, and lithium salts of carboxylic acids will dissolve in a polar solvent such as water or alcohol, thus permitting the contact desired to effect reaction. Accordingly, the carboxylic acid 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 metal salt of acyloxy carboxylic acid. The reactions proceed smoothly and efficiently at a temperature of about 20° to about 100° C. The amounts of reactants necessary to produce the metal salt of acyloxy carboxylic acid are not critical and can be varied widely, although it is sometimes desirable that an excess of the starting carboxylic acid salt be present.

Generally, the addition of about 0.5 to about 20 per cent by weight, and preferably from about 1.0 to about 10 per cent by weight, of the metal salt of acyloxy carboxylic acid, based on the lubricant, is sufficient to effect the desired improvement in the lubricant. Of the metal salts of acyloxy carboxylic acids which can be incorporated in lubricating oils in accordance with our invention, we can obtain good results with the salts of calcium, barium, zinc, nickel, and lead. Especially good results have been obtained with the calcium salt of acyloxy carboxylic acid.

The following example shows the preparation of the calcium salt of naphthenoyloxypropionic acid which is representative of the metal salts of acyloxy carboxylic acids which can be incorporated in lubricating oils to improve their detergency in accordance with our invention.

EXAMPLE 1

The sodium salt of naphthenic acids was prepared by reacting 1908 grams of naphthenic acids, having boiling points ranging from 155° to about 171° C. at 0.3 millimeters of mercury and having molecular weights ranging

from about 250 to 272, with a molar equivalent of sodium hydroxide in 5 liters of water. To the mixture at a temperature of about 30° C., a molar equivalent of beta-propiolactone was added with vigorous stirring. A maximum temperature of about 47° C. was reached about 15 minutes after the beta-propiolactone was added, and the solution became cloudy. After standing overnight, the mixture was cream colored and more viscous. To obtain a clear solution, the mixture was diluted with an equal volume of water and heated to boiling. A hot water solution of 497 grams of calcium chloride was added and a viscous precipitate formed immediately. After settling the water was decanted and the still wet calcium salt was dissolved in hexane. The hexane solution was water washed to remove the inorganic salts, such as sodium chloride and calcium chloride, after which the hexane solution was heated under reduced pressure to remove the solvent therefrom. The product obtained was a clear amber colored, semisolid, consisting essentially of the calcium salt of naphthenoyloxypropionic acid.

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

EXAMPLE 2

A mineral oil containing about 9.4 per cent by weight of the calcium salt of naphthenoyloxypropionic acid and analyzing 0.76 ash as calcium oxide was prepared. The oil analysis of the base oil and the blend were as follows:

	Base Oil	Blend
Gravity, °API	28.4	25.3
Viscosity, SUS:		
100° F	450	703
130° F	206	312
210° F	61	77.8
V. I.	98	106
Flash Point, ° F	485	425
Fire Point, ° F	550	535
Pour Point, ° F	−5	0
Color (NPA)	3	3
Sulfur, Percent	0.19	0.20
Carbon Residue, Percent	0.08	1.56
Ash, Percent (CaO)	0.01	0.76

The blend of mineral oil and detergent was tested in accordance with the S/C Lauson (diesel procedure) test, and the results are tabulated below in Table I:

Table I

Hours	Piston Varnish Rating	No. of Stuck Rings
24	10	0
48	10	0
72	10	0
96	10	0
120	10	0
144	10	0
168	10	0
192	10	0
216	10	0

The S/C Lauson (diesel procedure) test employed in Table I is conducted in the following manner. A single-cylinder Lauson engine developing 3 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 deposit 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 occurs earlier in the test.

The results set forth in Table I show clearly the effectiveness of the calcium salt of naphthenoyloxypropionic acid as a detergent in mineral oils. At the end of the test period of 216 hours, the piston varnish rating was 10, indicating little or no 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.

The following example also shows the improved detergency properties of a different base oil of the type employed in Example 1 having incorporated therein the calcium salt of naphthenoyloxypropionic acid:

EXAMPLE 3

A mineral oil containing 8.6 per cent by weight of the calcium salt of naphthenoyloxypropionic acid and analyzing 0.7 weight per cent ash as CaO was prepared. The oil analysis of the base oil and the blend were as follows:

	Base Oil	Blend
Gravity, °API	27.8	25.3
Viscosity, SUS:		
100° F	457	596
130° F	208	264
210° F	60.8	69.1
V. I.	95	99
Flash Point (C. O. C.), °F	470	340
Fire Point (C. O. C.), °F	545	535
Pour Point, °F	+5	0
Color (NPA)	3½	3½
Sulfur, percent	0.22	0.2
Carbon Residue, percent	0.07	1.48
Ash, percent (CaO)	<0.01	0.7

The blend of mineral oil and detergent was tested in accordance with the S/C Lauson (diesel procedure) test, and the results are tabulated below in Table II:

Table II

Hours	Piston Varnish Rating	No. of Stuck Rings
24	10	0
48	10	0
72	10	0
96	10	0
120	10	0
144	10	0
168	10	0
192	9+	0
216	9+	0

In this test there were no stuck rings at the end of the test period of 216 hours, while the piston varnish rating was 10 at the end of 168 hours, indicating no deposits of varnish, and 9+ at the end of the test period of 216, indicating only very slight deposits of varnish.

While in Example 1 we have used beta-propiolactone in the preparation of the calcium salt of naphthenoyloxypropionic acid, we can use a beta-halopropionic acid, such as beta-chloropropionic acid, in its preparation without affecting the composition or structure of the salt of the acyloxy propionic acid obtained. Similarly, if desired, we may 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 an acyloxy acetic acid derivative would be obtained instead of an acyloxy propionic acid derivative.

Although we prefer to employ carboxylic acids such as naphthenic acids in the preparation of the metal salts that are to be incorporated in lubricating oils in accordance with our invention, we can also use other acids such as sulfonic acids and mixtures of mono and di-isooctyl ortho phosphoric acids in their preparation and

still obtain suitable reaction products whose metal salts can be incorporated in lubricating oils.

In preparing the improved 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 a metal salt of an acyloxy carboxylic acid, 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 a relatively small amount of a metal salt of an acyloxy carboxylic acid 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.

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 comprising a major amount of a lubricating oil and a minor amount sufficient to improve the detergency characteristics thereof of a metal salt of a naphthenoyloxypropionic acid.

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 of naphthenoyloxypropionic acid where said metal is selected from the group consisting of calcium, barium, zinc, nickel and lead.

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 calcium salt of napththenoyloxypropionic acid.

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