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LUBRICATING OIL COMPOSITIONS

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This invention relates to new lubricating oil compositions and in particular concerns lubricating oil compositions having improved properties of detergency and oxidation stability.

At the present time it is common practice to enhance or modify certain of the properties of lubricating oils through the addition of various improvement agents or additives. The lubricating oils employed in internal combustion engines, such as automotive, aviation and Diesel engines, in particular require the use of additive agents to render them serviceable under the extreme conditions of pressure and temperature encountered in this type of engine. Among the several shortcomings of uncompounded mineral oils when used as lubricants in such engines, one of the most serious is manifested by sludge formation in the crankcase, sticking of the piston rings, and the formation of varnish-like coatings on the pistons and cylinder walls. These difficulties are all considered to be due to oxidation of the oil under operating conditions whereby there is formed a variety of oxidation products which range in physical form from a soft sludge, such as accumulates in the crankcase, to a hard adhesive deposit which accumulates in back of the piston rings causing them to stick with consequent inadequate lubrication of the cylinder walls, scoring of the cylinder walls, overheating, loss of power, etc. These difficulties may be alleviated by adding to the oil minor amounts of certain agents which apparently act to disintegrate and colloidal disperse the sludge throughout the oil and thus prevent it from accumulating at any one point in the lubrication system. Since this action is somewhat akin to the action of detergents in aqueous media, the agents so employed are termed "detergent additives" although they are quite different chemically from the water-soluble detergents or dispersing agents commonly used in aqueous cleansing operations. In some instances these additives may also act to increase the oxidation stability of the oil, and thus serve the additional purpose of decreasing the amount of oxidation products formed in the oil.

While a number of chemical products have been proposed for use as detergent additives in compounded lubricating oil compositions, many of such products have not proved sufficiently effective for use in the more modern types of engines. Others satisfactorily effect the desired detergent action, but at the same time disadvantageously alter the physical properties of the oil. Still others interfere with the action of other additives, e. g., anti-corrosion agents, pour-point depressants, ex-

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treme pressure agents, viscosity index improvers, etc., or must be employed in such quantity as to increase unduly the cost of the oil.

It is accordingly an object of the present invention to provide lubricating oil compositions having improved detergent properties.

Another object is to provide lubricating oil compositions containing minor amounts of detergent additives which do not adversely affect the desirable properties of the oil and which do not interfere with the action of other additive agents.

A further object is to provide lubricating oil compositions which will substantially reduce ring-sticking and attendant difficulties in internal combustion engines, particularly those of the Diesel type.

Other objects will be apparent from the following detailed description of the invention, and various advantages not specifically referred to herein will occur to those skilled in the art upon employment of the invention in practice.

In accordance with the above and related objects, I have found that certain metal salts of naphthenoxy-stearic acids have properties which render them admirably suited for use as detergent additives in lubricating oil compositions. More particularly, I have found that the polyvalent metal salts of naphthenoxy-stearic acids may be incorporated with mineral oils of lubricating viscosity to form lubricating compositions which substantially reduce ring-sticking when employed in modern internal combustion engines, including Diesel engines. Such salts are effective in relatively small amounts so that their presence in the composition does not materially affect the physical properties of the oil or interfere with the action of other additive agents which may be included in the composition.

The term "naphthenoxy" as herein employed refers to the group $R-COO-$, derived from a naphthenic acid, $R-COOH$, wherein R represents a naphthenic hydrocarbon radical, just as the term "acetoxy" refers to the group CH_3COO- , derived from acetic acid, CH_3COOH . The naphthenoxy-stearic acids are thus stearic acids having an $R-COO-$ group substituted at some point along the aliphatic chain. They are obtained by esterifying naphthenic acids with any of the isomeric hydroxy-stearic acids, or mixtures thereof, in accordance with ordinary esterification procedure. As ordinarily obtained employing a commercial grade of the naphthenic acids in the esterification reaction, they are high-boiling dark-colored oily liquids, soluble in a variety of organic solvents. If desired, they

may be purified prior to use in forming the metal salts employed in accordance with the invention, but it is usually more convenient and economical to employ them in crude form directly as they are obtained from the esterification reaction.

The polyvalent metal salts of the naphthenoxy-stearic acids are conveniently prepared by metathesis from the corresponding sodium or other alkali-metal salt. In preparing the intermediate alkali-metal salt, the naphthenoxy-stearic acid is preferably first dissolved in an inert reaction medium, such as acetone, ethanol, etc., and the alkali-metal is employed in the form of an alcoholate, such as sodium methylate, potassium ethylate, etc., or as an alcoholic solution of the hydroxide. The reaction takes place readily upon mixing the two reactants at room temperature or slightly above. If desired, the alkali-metal naphthenoxy-stearate product may be isolated and thereafter dissolved in water and reacted with an aqueous solution of a salt of the desired polyvalent metal to form the corresponding polyvalent metal naphthenoxy-stearate, but ordinarily it is more convenient simply to add water to the reaction mixture, and then add the aqueous polyvalent metal salt solution. The double decomposition reaction takes place readily at ordinary temperatures, and the polyvalent metal naphthenoxy-stearate precipitates out of solution, and may be separated and washed free of soluble contaminants. Any water-soluble polyvalent metal salt may be employed to obtain the corresponding metal naphthenoxy-stearate in this manner, e. g., barium chloride, calcium chloride, zinc nitrate, ferric chloride, strontium nitrate, aluminum sulphate, magnesium bromide, manganese chloride, lead nitrate, copper sulphate, chromium chloride, antimony chloride, cobalt nitrate, nickel chloride, cadmium nitrate, tin chloride, etc., and any of the oil-soluble metal salts so obtained may be used in accordance with the invention. By reason of their general availability and low cost, the metals of groups II and VIII of the periodic system are usually preferred.

In compounding the improved lubricating oil compositions provided by the invention, the desired metal naphthenoxy-stearate is added to the base oil in an amount sufficient to secure the desired degree of improvement in the service characteristics of the oil. This amount will accordingly depend upon the characteristics of the oil itself, as well as upon the conditions to which the composition is subjected in use. Ordinarily, however, the metal salt additive is employed in an amount representing between about 0.1 and about 5.0 per cent by weight of the entire composition. If the composition is to be employed in more or less light-duty operations, e. g., in automobile engines, the amount of the additive is usually at the lower end of this range, whereas compositions to be used in heavy-duty gasoline or Diesel engines will contain somewhat larger proportions of the additive. The base oil may be any hydrocarbon oil of lubricating grade and viscosity obtained by any of the modern refining methods from paraffinic, naphthenic, asphaltic, or mixed base stocks, or it may be a synthetic lubricating oil produced, for example, by the polymerization of olefins.

As previously stated, the detergent additives of the present invention function independently of other types of additives without materially altering the physical characteristics of the oil. Accordingly, the base oil may contain other additive agents, such as viscosity index improvement

agents, pour-point depressants, bearing corrosion inhibitors, oxidation inhibitors, extreme pressure agents, anti-foam agents, etc. The nature of such additives and the proportion in which they are employed, as well as the characteristics of the base oil itself, will depend upon the use to which the composition is to be put, and the selection and compounding of base oils to provide compositions adapted for specific uses will be understood by those skilled in the art.

The following examples will illustrate several ways in which the principle of the invention has been applied, but are not to be construed as limiting the same. All proportions are by weight.

Example I

Naphthenoxy-stearic acid was prepared by dissolving 300 parts of hydroxy-stearic acid, 250 parts of a naphthenic acid having a neutralization equivalent of 200, and 5 parts of p-toluene-sulfonic acid in 173 parts of toluene. This mixture was heated at reflux temperature for 24 hours, during which time 16 parts of water formed in the reaction were recovered. The mixture was then treated with anhydrous sodium carbonate to neutralize the acid catalyst, and the solids were filtered off. After distilling off the toluene, the naphthenoxy-stearic acid was obtained as a dark-colored high-boiling oily liquid. This product was diluted with about $\frac{1}{4}$ of its volume of acetone, and 68 parts of sodium ethylate dissolved in ethyl alcohol were added with stirring, whereby there was formed a brown precipitate of sodium naphthenoxy-stearate. Sufficient water was added to the mixture to dissolve this precipitate, and 150 parts of nickel nitrate dissolved in water were added with stirring, whereby there was formed a dark precipitate of nickel naphthenoxy-stearate. The supernatant liquid was decanted and the precipitate was dissolved in hexane and washed with water. It was recovered as a greenish-brown viscous liquid by evaporating off the hexane. It contains 5.5 per cent nickel by analysis. A lubricating oil composition typical of those provided by the invention was prepared by dissolving 3.3 parts of the nickel naphthenoxy-stearate in 96.7 parts of a solvent-refined Mid-Continent oil. The physical properties of this composition, together with those of the base oil, were as follows:

	Base Oil	Base Oil+ 3.3% Additive
Gravity, °API.....	26.5	27.7
Viscosity, SUS at—		
100° F.....	463	508
130° F.....	206	224
210° F.....	59.9	62.4
Viscosity Index.....	88	90
Flash Point, °F.....	470	470
Fire Point, °F.....	525	530
Pour Point, °F.....	+20	+5
Color, N.P.A.....	2+	3.5-
Carbon Residue.....	0.05	0.29
Neutralization Number.....	0.01	0.06
Ash, Per Cent.....	0.01	0.20

This composition was tested in a standard Lauson engine for ability to prevent ring-sticking. The Lauson test consists in placing 2.1 lbs. of the composition in the crankcase of a single cylinder Lauson Diesel engine. The engine is operated under a 3 H. P. load at 1850 R. P. M., maintaining a cooling jacket temperature of 300° F., an oil temperature of 225° F., and an air-to-fuel ratio of 13:1. At the end of 24 hours operation, the engine is stopped, disassembled, and the piston is examined as to stuck rings and discolora-

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tion. If there are no stuck rings, the engine is reassembled, the oil charge is brought up to 2.1 lbs., and operation is continued for another 24-hour period. This procedure is repeated until one of the rings sticks or until a total of 216 operating hours has accrued. The piston color is rated on an arbitrary scale of 10 to 0 representing increasing discoloration of the piston skirt. The data obtained in this test, together with comparative data on the base oil is tabulated as follows:

Length of Test, Hrs.	Base Oil		Base Oil+ Additive	
	Piston Color	No. of Stuck Rings	Piston Color	No. of Stuck Rings
24	2	0	9	0
48	1	1	9	0
72	---	---	9	0
96	---	---	9	0
120	---	---	8+	0
144	---	---	8+	0
168	---	---	8+	0
192	---	---	8+	0
216	---	---	8+	0

Example II

A lubricating oil composition similar to that described above in Example I but containing only 1.7 per cent of the nickel naphthenoxy-stearate was found to be equally effective in preventing ring-sticking in the Lauson engine test. With a third composition containing 0.83 per cent of the additive, ring-sticking occurred only after 120 hours of operation in the Lauson engine.

While the compositions described above were formulated for testing purposes, and thus contained only the base oil and the polyvalent metal naphthenoxy-stearate additive, it will be understood that compositions for various commercial applications will usually also contain other additive agents, particularly oil-soluble corrosion inhibitors. The following examples are illustrative of such multi-component compositions:

Example III

	Per cent
Pennsylvania paraffin-base oil, SAE 20	97.45
Calcium naphthenoxy-stearate	2.5
Cyclohexylamine oleate	0.05

In this composition, the cyclohexylamine oleate serves as a corrosion inhibitor.

Example IV

	Per cent
Mid-Continent paraffin-base oil, SAE 40	94.9
Barium naphthenoxy-stearate	3.6
Refined sulfurized sperm oil	1.5

In this composition, the sulfurized sperm oil serves as a combined extreme pressure agent and corrosion inhibitor.

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Example V

	Per cent
Mid-Continent paraffin-base oil, SAE 30	98.4
Chromic naphthenoxy-stearate	1.5
Tri-orthocresyl-phosphite	0.1
Poly-dimethyl-silicone	0.001

In this composition, the tri-orthocresyl-phosphite serves as a bearing corrosion inhibitor, and the poly-dimethyl-silicone serves as an anti-foam agent.

Example VI

	Per cent
Paraffin base oil, SAE 20	95.5
Zinc naphthenoxy-stearate	1.5
Aluminum naphthenoxy-stearate	1.5
Refined sulfurized sperm oil	1.5
Poly-dimethyl-silicone	.001

Example VII

	Per cent
California naphthenic oil, SAE 30	97.5
Cadmium naphthenoxy-stearate	1.0
Nickel naphthenate	1.0
Chlorinated paraffin	0.5

In this composition, the chlorinated paraffin serves as an extreme pressure agent, and the nickel naphthenate serves as a bearing corrosion inhibitor.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made in the ingredients or proportions thereof, provided the compositions stated by any of the following claims be obtained.

I, therefore, particularly point out and distinctly claim as my invention:

1. A lubricating oil composition essentially comprising a major proportion of a hydrocarbon oil of lubricating viscosity and between about 0.1 and about 5.0 per cent by weight of the composition of an oil-soluble polyvalent metal salt of naphthenoxy-stearic acid.

2. A lubricating oil composition according to claim 1, wherein said metal is selected from the class consisting of the metals of groups II and VIII of the periodic system.

3. A lubricating oil composition according to claim 1, wherein said salt is a nickel naphthenoxy-stearate.

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