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3,454,497

LUBRICATING COMPOSITIONS

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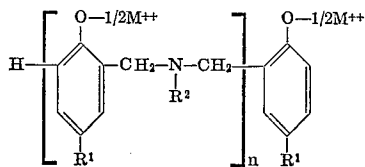
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5 Claims

ABSTRACT OF THE DISCLOSURE

Lubricating oil compositions are disclosed. These compositions comprise a compound of the formula

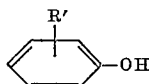


wherein R^1 and R^2 are aliphatic hydrocarbon radicals, n is an integer from 1 to 50, and M is an alkaline earth metal.

This invention relates generally to lubricating oil compositions. In particular, the invention relates to a multi-function polymeric additive which serves as an antioxidant and dispersant for lubricating oil and to lubricating compositions containing the polymeric additive.

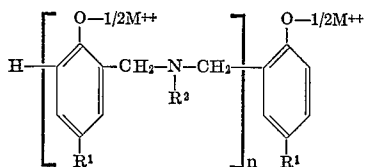
Dispersant or detergent additives and antioxidant additives for lubricating oils are well known. In the area of heavy-duty lubricants for the lubrication of, for example, diesel truck engines, wherein high temperatures are encountered for substantial periods of time in addition to the usual stop-and-go driving which is found in traffic, there is a continuing demand to provide improved lubricants of longer life and lubricants which reduce engine wear and maintenance.

It has now been found that lubricating oil compositions possessing good antioxidant and dispersant properties are provided by incorporating therein a minor amount of the oil-soluble polymeric additive of the present invention consisting of a metal phenate prepared by reacting a metal hydroxide with a product prepared from a phenol of the general formula



formaldehyde; and an alkylamine of the formula R^2NH_2 . R^1 is preferably an alkyl group of from 1 to 20 carbon atoms, and most preferably a C_{8-20} alkyl group, such as octyl, decyl, dodecyl, hexadecyl, and the like. R^2 is preferably an alkyl group of from 1 to 4 carbon atoms, such as methyl, ethyl, or isopropyl.

Although the structure of the additive is not known with absolute certainty, it is believed to have the following formula:



wherein M is preferably an alkaline earth metal and most preferably, calcium; n is an integer from 1 to 10 or higher, e.g., 20 or 50, but preferably is from 2-7; and R^1 and R^2 are as previously defined.

The base oil used to form the compositions of the pres-

2

ent invention can be a mineral lubricating oil obtained from paraffinic, naphthenic, asphaltic or mixed base crudes and/or mixtures thereof, for example a neutral lubricating oil having a viscosity which may vary over a wide range such as from 100 to 6500 SSU at 100° F. Under extreme engine operating conditions it is desirable to use an oil blend containing from 1 to 20% of bright stock. This oil fraction is a viscous product obtained by dewaxing or treating with fuller's earth distillation residues after the volatile fractions have been removed. The viscosity of bright stocks vary from 80 to 250 SSU at 210° F. and range in molecular weight from 500 to 2000 or higher. In addition to mineral lubricating oils, the polymeric additives may be incorporated into synthetic lubricating oils such as polymerized olefins, silicone polymers, esters and ethers. Mixtures of natural and synthetic oils can also be used.

Mineral lubricating oils particularly useful are in the viscosity range of from 100 to 1200 SSU at 100° F. and have a viscosity index of 90 to 115.

The polymeric additive of this invention can be used effectively in any of the above oily media in amounts of from 0.1% to 10% and preferably from 2% to 5%, although amounts as large as 20% by weight may be used, if desired.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood that the examples are for purposes of illustration and the invention is not to be regarded as limited to any specific embodiment recited therein.

EXAMPLE I

This example illustrates the preparation of the polymeric additives of the present invention.

A 2-liter flask was charged with 260 g. (1 mole) dodecylphenol dissolved in 500 ml. of absolute methanol and 77.5 g. of 40% wt. aqueous methylamine (1 mole CH_3NH_2). The mixture was stirred and the temperature was maintained at 25-30° C. while 162 g. of 37% wt. aqueous formaldehyde (2 moles CH_2O) was added dropwise during one hour. When the addition was nearly complete, the clear pale yellow solution became cloudy and a second phase separated. The mixture was stirred and heated to reflux for 3 hours then cooled to room temperature. The upper methanol/water phase was decanted from the yellow viscous polymer layer that had formed. The polymer was dissolved in 500 ml. benzene and washed four times with 300 ml. portions of water. The wet benzene solution was stirred and refluxed with a mixture of 40.7 g. (1.1 equivalents) calcium hydroxide and 200 ml. methanol for 2 hours. The methanol was then removed by distillation and the residue was dried by azeotropic distillation with benzene. The residue was filtered hot and the filtrate was diluted with 306 g. of HVI (high viscosity index) 100 N (neutral) base stock oil. The solution was stripped with nitrogen under vacuum until all the benzene was removed. A yield of 612 g. of a 50% wt. additive concentrate in oil (Additive A) was recovered. Polymeric Additive A has three recurring units, i.e., in the above formula n is 3.

The above procedure may be used with other starting materials to prepare similar type polymers, for example, instead of dodecylphenol, octyl-, hexadecyl-, or decylphenol can be employed; also ethyl-, isopropyl- or butylamine can be used in place of methylamine. Moreover, other metal hydroxides may be used such as barium hydroxide without significantly altering the characteristics of the polymer.

EXAMPLE II

This example compares the antioxidant activity and dispersancy life of the polymeric additive of the present in-

vention with that of other known additives under the same conditions.

In the following table Additive A is the additive prepared in Example I; Additive B is the calcium salt of the condensation product of formaldehyde and octylphenol and has a sulfated ash content of 8.0% w. Additive C is the calcium salt of the condensation product of formaldehyde and dodecylphenol; Additive D is sulfurized calcium alkyl phenate; Additive E is sulfurized calcium octyl phenate; Additive F is sulfurized calcium dodecyl phenate. Each additive was blended in HVI 100 N base stock oil at 0.2% wt. sulfated ash to form Compositions A through F, respectively, and tested in the 300° F. Air Oxidation Test in the presence of 20 p.p.m. iron and 20 p.p.m. copper as catalysts. In the test, a stream of air (30 ml./min.) was bubbled through a 20-gram sample of lubricant (oil composition) in the presence of said catalysts. The induction period, which is the length of time elapsed before a substantial increase in the rate of oxygen-uptake occurs, is a standard measure of oxidation stability and is given for each additive in the table below. Each additive is also subjected to the blotter spot life test which is indicative of dispersancy life. In this latter test a drop of the oil composition is placed on a blotter at regular intervals and the spot formed examined. The time required for undispersed insolubles to appear in the spot is recorded and given in Table I below.

TABLE I

Additive	Induction period, hr.	Blotter spot life, hr.
None.....	0	0-10
A.....	52	>72
B.....	11	0-8
C.....	13	0-8
D.....	3	6-14
E.....	6	6-14
F.....	4	6-14

The results of the tests establish that with the additive of the present invention the induction period was three times longer than the next best additive (B) and the dispersancy life was five times longer than the next best (D, E or F).

EXAMPLE III

In this example Additive A and Additive B are compared and evaluated in a Caterpillar 1-G test. The test engine is the single cylinder, 4 cycle, Caterpillar Diesel Lubricant Test Engine converted to a 5½ in. bore and 6½ in. stroke engine. In general the test conditions are:

Oil change	hr.	120
Engine speed	r.p.m.	1800
Fuel rate	B.t.u./min.	5850
Load, b.m.e.p.	p.s.i. Approx.	141
Air to engine temperature	° F.	255
Air to engine pressure	in. Hg abs.	53
Water outlet temperature	° F.	190
Oil sump temperature	° F.	205
Fuel sulfur content	percent min.	0.35

The test is described in detail in Federal Test Method Standard No. 791 Method 341-T.

To evaluate Additive A and compare it to Additive B the following lubricant compositions were prepared.

Ingredient:

HVI 100 N	parts by weight	5.0
HVI 250 N	do.	53.1
HVI 150 bright stock	do.	15.0
Calcium sulfonates in HVI 250 N	do.	23.6
Additive A (5.89% w. sulfated ash)	do.	13.3

Plus

Pour depressant and viscosity improver (methacrylic polymer 34% in oil; 50% cetyl-, 25% lauryl- and 25% octyl methacrylate)	parts by weight	0.06
Antioxidant (phenyl-alpha-naphthyl-amine)	percent	0.20
Antifoamant (silicone polymer)	p.p.m.	10

¹ Or 0.2% w. sulfated ash.

The above composition is designated as Composition A. A composition designated as Composition B was prepared which was identical to Composition A with the exception that the equivalent amount, 2.5 parts by weight (or 0.2% w. sulfated ash), of Additive B was incorporated into the composition instead of 3.3 parts by weight of Additive A. Compositions A and B were evaluated and compared in the Caterpillar 1-G Test and the results of the tests are given in Table II. In order to more vividly demonstrate the superiority of Additive A over Additive B, Composition A was tested for 480 hours while Composition B was tested for only 240 hours.

TABLE II

	Composition A, 480 hrs.	Composition B, 240 hrs.
Percent top ring groove filling	35	56
Percent carbon in second ring groove	2	4
Lacquer, area covered, percent ring lands:		
No. 1	20	46
No. 2	0	0
No. 3	0	0
Third ring groove	0	0
Skirt	0	0
Undercrown	0	50

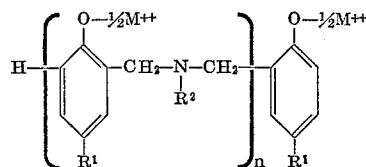
The results in Table II show that Composition B failed the test (more than 50% top ring groove filling) after only 240 hours. Composition A containing Additive A passed the test and had a better rating after 480 hours than Composition B containing Additive B had after 240 hours.

The polymeric additive of this invention can be combined with other additives in lubricants, such as other antioxidants and dispersants, if desired, corrosion inhibitors, or anti-rusting compounds, wear inhibitors, blooming agents, pour point depressants, viscosity improvers, anti-forming agents, e.g., dimethyl silicone polymer, and the like. Depending upon the primary additives used and conditions under which they are used, the amount of secondary additives used may vary from 0.01% to 2% or higher, e.g., to 5-10%.

The polymeric additive of this invention is particularly useful in heavy-duty oils and can also be used in turbine oils, gear oils, and in various other fields of lubrication where detergency and oxidation stability properties are desirable.

I claim as my invention:

1. A lubricating composition comprising a major amount of a lubricating oil and from 0.1-20% by weight of a compound of the formula:



wherein R¹ and R² are aliphatic hydrocarbon radicals, n is 3, and M is an alkaline earth metal.

2. A composition as defined in claim 1 wherein R¹ is a C₈-20 alkyl group, R² is a C₁-4 alkyl group, and M is calcium.

3. A composition as defined in claim 1 wherein the oil is a mineral oil.

4. A composition as defined in claim 1 wherein R¹ is dodecyl, R² is methyl, and M is calcium.

5. A composition as defined in claim 4 wherein the oil is a mineral oil.

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