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AMINES AS ANTIWEAR ADDITIVES IN MARINE CYLINDER OILS

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No Drawing. Continuation-in-part of application Ser. No. 807,087, Mar. 13, 1969. This application Apr. 15, 1971, Ser. No. 134,437

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U.S. Cl. 252—42.7 4 Claims

ABSTRACT OF THE DISCLOSURE

Combinations of overbased calcium phenates and relatively high molecular weight aliphatic hydrocarbon substituted alkylene polyamines are used in lubricating oils, particularly marine lubricating oils, to reduce wear and provide acid neutralization capacity.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 807,087, filed Mar. 13, 1969, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

Rusting and acidic corrosion may result in severe wear of engine parts. This type of corrosive wear is particularly common in situations where water is present. Common additives which are found effective to reduce this wear are alkaline additives, such as the phenates, and basic sulfonates. These basic additives, by maintaining the pH at neutral or above, prevent acidic corrosion of the metallic parts of the engine. Therefore, the basic additives are considered solely to function as acid neutralizers in preventing corrosive wear.

Description of the prior art

Phenates are commonly used additives in lubricating oils, particularly as overbased phenates, wherein calcium carbonate or other calcium base is dispersed in an oil medium by alkylphenol salts or polyalkylphenol salts, being bridged either with methylene groups or sulfur. Illustrative overbased phenates may be found in U.S. Pats. Nos. 3,336,224, 3,178,368, 3,036,971, 2,680,096 and 3,367,867.

Recently, relatively high molecular weight aliphatic hydrocarbon substituted alkylene polyamines have been reported as detergents for lubricating oils and also having wear-inhibiting properties. These compositions are found in U.S. Pat. No. 3,275,554.

SUMMARY OF THE INVENTION

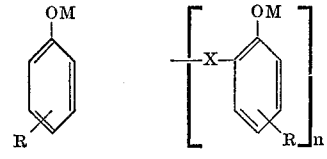
Wear-reducing lubricating oil compositions are provided having alkalinity values of from 8 to 80 mg. KOH/g. and being a combination of overbased calcium phenates and long chain aliphatic hydrocarbon substituted alkylene polyamines, wherein the contribution of alkalinity value of the phenate to the polyamine is in the ratio of 3–12:1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Lubricating oil compositions are provided having alkalinity values of from 8 to 80 mg. KOH/g., and containing calcium overbased phenates and aliphatic hydrocarbon substituted alkylene polyamines, wherein the ratio of contribution of alkalinity value of the overbased phenates to the aliphatic hydrocarbon substituted alkylene polyamines is in the range 3–12:1, preferably 4–10:1.

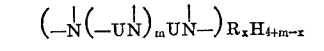
The concentration of overbased phenates (including calcium carbonate or other calcium base) in the lubricating oil composition will generally be 2 to 20 weight percent, more usually 4 to 15 weight percent. In proportion, the aliphatic hydrocarbon substituted alkylene polyamine will be present in amounts of from 0.5 to 5 weight percent, more usually from 1 to 4 weight percent.

Turning now to a consideration of the individual components of the lubricating composition. The phenates will for the most part have the following formula:



wherein M is hydrogen or calcium, when calcium, its second valence may be satisfied by a phenoxide, alkoxide or hydroxide, X is methylene, thio or polythio having from 2 to 3 sulfur atoms, R is straight or branched chain alkyl groups of from 8 to 35 carbon atoms and *n* is an integer of from 0 to 2. X is normally bonded at the position ortho to the oxygen. As already indicated, the methods of preparing the various phenates are well known in the art and do not require exemplification here. In combination with the phenate will be calcium either as the hydroxide, lower alkoxide or carbonate, preferably carbonate. Normally the calcium is excess of the amount necessary to neutralize the alkyl phenol will be present in a mole ratio of from 1–4:1.

The aliphatic hydrocarbon substituted alkylene polyamine will generally have the following formula:



wherein R is an aliphatic hydrocarbon of from 18 to 200 carbon atoms, U is alkylene of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, *m* is an integer of from 0 to 5 and *x* is an integer of from 1 to 3. Preferred R groups are polymers of low molecular weight olefins of from 2 to 6 carbon atoms, particularly the branched chain olefins of from 3 to 4 carbon atoms, i.e., propylene and isobutylene. Illustrative of alkylene polyamines are ethylene diamine, propylene diamine, diethylene triamine, tetraethylene pentamine, tripropylene tetramine, etc.

The lubricating oils which find use will be hydrocarbon lubricating oils which may be paraffin-based, naphthenic-based, asphaltic-based or mixed based oils. The lubricating oils generally have viscosities in the range of 35 to 50,000 Saybolt Universal seconds (SUS) at 100° F. These oils which find particular use as marine lubricating oils will generally have viscosities in the range of 50 to 150 SUS at 210° F. They are low viscosity index oils having viscosity indexes in the range of about 50 to 120 V.I. and are derived primarily from aliphatic and naphthenic stocks.

In order to demonstrate the effectiveness of the subject compositions, a number of compositions were prepared having varying hydrocarbon polyamines and varying amounts of an overbased sulfurized alkylphenate, The overbased sulfurized alkylphenate was prepared as described in U.S. Pat. No. 3,367,867. In order to evaluate the effect on wear of the various compositions, the following test was carried out.

A Ruston Hornsby Engine Model HRD No. 3, a 4-cycle diesel, was used. The fuel employed had the following inspections: gravity, degree API 25.6; viscosity, SUS at 100° F., 52; sulfur, weight percent, 3.44. The engine is operated under the following conditions: speed, 400 r.p.m.; air inlet temperature, 100° F.; water inlet temperature, 130° F.; water outlet temperature, 140° F.; fuel flow rate, 50 mm. per second; top cylinder oil (test oil) flow rate, 26 drops per minute.

The Ruston Hornsby diesel engine utilizes four piston rings which are weighed individually and the weight recorded. The rings are installed on the piston, the engine is installed, and a 20-hour break-in period is employed. The rings are weighed at the end of the 20 hours and the total weight recorded. The engine is then run for an additional 40 hours (a total of 60 hours) and the pistons removed and weighed. The weight loss is determined as that amount which occurred in the last 40 hours. The reference oil composition is normally run before and after the test oil and the average wear value for the two reference runs is used for comparison. This average is used since the wear rate is subject to variation. However, since the variations occur by a relatively constant trend, the bracketing of the test oils with reference oil wear level data allows a determination of the test oil's capabilities as a wear reduction agent vis-a-vis the reference oil.

The base oil employed was a 60 V.I. diesel engine lubricating SAE 30 base oil. Polyamine and overbased phenate were employed to provide various alkalinity values and the wear rates determined. The reference oil used for comparison in each run was the above base oil containing the overbased phenate in an amount to provide an alkalinity value of 20 except where otherwise indicated in Table I. The alkalinity value is reported as mg. KOH per gm. of sample and is determined at a methyl red end point, so that all carbonate and carboxylates are titrated. The following table indicates the results obtained.

TABLE I

Amine [1] conc. A.V.	Phenate conc. A.V.	Wear rate, mg./hour Reference	Wear rate, mg./hour Test	Wear ratio test/ reference	Percent reduction [2] in ring wear
	20	6.9	6.1	0.88	12
A 10	20	5.3	3.2	0.60	40
	30				
A 2	20	11.8	5.8	0.49	51
	20				
B 2	20	6.2	4.0	0.65	35
	20				
B 4	20	10.8	5.1	0.47	54
	20				
A 2	10	12.4	10.4	0.84	16
	8				
B 2	10	12.4	8.9	0.72	82
	8				

[1] A—Polyisobutenyl (≃450 av. mol. wt.) diethylene triamine; B—polyisobutenyl (≃1,000 av. mol. wt.) tetraethylene pentamine.

[2] % Reduction in ring wear defined as:

[Difference in weight loss (Ref-Test) ×100] ÷ Weight Loss Reference

It is evident from the foregoing results, that by using combinations of hydrocarbon polyamines and calcium bases, great wear reductions can be achieved at relatively low alkalinity values. Significant enhancement of the effect of reduction wear is obtained by employing small amounts of an aliphatic hydrocarbon substituted alkylene polyamine in combination with relatively larger amounts of overbased phenates containing calcium salts as a base source.

What is claimed is:

1. A lubricating oil composition having improved antiwear properties having a major amount of an oil of lubricating viscosity and from 2 to 20 weight percent of an overbased calcium phenate and from 0.5 to 5 weight percent of an aliphatic hydrocarbon substituted alkylene polyamine, wherein said aliphatic hydrocarbon group is of from 18 to 200 carbon atoms and the alkylene polyamine group has from 2 to 6 nitrogen atoms.

2. A lubricating oil composition according to claim 1, wherein said lubricating oil has a viscosity in the range of 50 to 150 SUS at 210° F.

3. A lubricating oil composition according to claim 2, wherein said aliphatic hydrocarbon substituted alkylene polyamine is polyisobutenyl ethylene diamine.

4. A lubricating oil composition according to claim 2, wherein said aliphatic hydrocarbon substituted alkylene polyamine is polyisobutenyl tetraethylene pentamine.

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U.S. Cl. X.R.

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