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MULTI-FUNCTIONAL LUBRICATING OIL ADDITIVES

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This invention relates to novel multi-functional lubricating oil additives. More particularly, this invention relates to lubricating oil additives which act as detergents, anti-oxidants and anti-corrosives.

We have found that minor amounts of divalent metal salts of N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acids having the following general formula

$$[R_2NCSS(CH_2)_xCOO]_2Z$$

wherein R represents an aliphatic hydrocarbon radical, x is at least 1 and Z represents a divalent metal, are excellent lube oil additives and act as anti-oxidants, anti-corrosives and detergents. The useful addition range of these compounds in a lube oil is from about 0.2 to 2.0% by weight; however, the preferred concentration is about 1%.

Examples of divalent metals which are used in the formation of the salts of N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acids are magnesium, zinc, barium, calcium, tin and strontium. Of these, the magnesium salt is preferred.

Specific examples of the various salts of N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acids which are useful in the present invention are magnesium N,N-dioctyl dithiocarbamyl acetate, magnesium N,N-di-2-ethylhexyl dithiocarbamyl acetate, magnesium N,N-dioctyl dithiocarbamyl laurate, magnesium N,N-dioctyl dithiocarbamyl stearate, magnesium N,N-diamyl dithiocarbamyl acetate, magnesium N-amyl-N-octyl dithiocarbamyl acetate, magnesium N,N-dibutyl dithiocarbamyl laurate, barium N,N-dioctyl dithiocarbamyl acetate, barium N-butyl N-hexyl dithiocarbamyl propionate, zinc N,N-di-2-ethylhexyl dithiocarbamyl propionate, tin N,N-diamyl dithiocarbamyl acetate, zinc N,N-dibutyl dithiocarbamyl acetate, zinc N,N-dioctyl dithiocarbamyl acetate, strontium N,N-dioctyl dithiocarbamyl acetate, calcium N,N-dioctyl dithiocarbamyl acetate, calcium N-amyl N-octyl dithiocarbamyl acetate, calcium N,N-di-2-ethylhexyl dithiocarbamyl butanoate, calcium N,N-dibutyl dithiocarbamyl stearate, zinc N,N-di-3-hexyldecyl dithiocarbamyl oleate, magnesium N-butyl N-2-ethyl-4-hexyldecyl thiocarbamyl acetate and magnesium N,N-di-2-methyl-4-butyldecyl thiocarbamyl acetate.

From the above examples it is apparent that the x in the general formula $[R_2NCSS(CH_2)_xCOO]_2Z$ can denote an integer from 1 to 20. However, acetates wherein x is 1 are the preferred class of compound on the basis of availability and cost. The aliphatic radicals on the nitrogen atom may contain 4 to 20 but usually have 6 to 12 carbon atoms.

We have also found that combinations of divalent metal salts of N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acids with the well known metal phenolate type detergents such as metal alkyl phenolates, metal alkyl salicylates, metal alkyl phenolate-sulfonates, metal alkyl phenolate-sulfides and disulfides serve as multi-functional lube oil additives having excellent detergent, anti-corrosive and anti-oxidant properties. The metals which are useful in forming these detergents are magnesium, zinc, barium and calcium. The alkyl group in these metal phenolates ranges from 4 to 30 carbon atoms.

The amount of these detergents which we have found to be useful in the combination, ranges from about 25 to 75% by weight of the divalent metal salt of the N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acid but we prefer from about 25 to 35% of the detergent in the mixture prior to its addition to the lube oil.

The combination additive comprising a divalent metal salt of an N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acid and a detergent from the above mentioned group is used in lube oils in a concentration range from about 0.5 to 2.5% by weight with about 1.5% preferred. Specific examples of salt-detergent combinations with their percentage composition are as follows: Magnesium N,N-di-2-ethylhexyl dithiocarbamyl acetate 67% and zinc alkyl salicylate 33% wherein the alkyl group comprises olefin polymers having an average of 25 carbon atoms; magnesium N-amyl N-octyl dithiocarbamyl propionate 75% and barium hexyl phenolate 25%; magnesium N,N-dioctyl dithiocarbamyl acetate 60% and zinc lauryl phenolate 40%; magnesium N,N-dioctyl dithiocarbamyl acetate 65% and calcium hexyl phenolate sulfonate 35%; calcium N,N-dioctyl dithiocarbamyl acetate 70% and zinc alkyl salicylate 30% wherein the alkyl group comprises olefin polymers having an average of 20 carbon atoms; and zinc N,N-dibutyl dithiocarbamyl laurate 63% and barium alkyl phenolate 37% wherein the alkyl group comprises olefin polymers having an average of 15 carbon atoms.

The salts of the N,N-dialiphatic dithiocarbamyl aliphatic carboxylic acids useful in the present invention may be formed by various reactions. One such method is given in the following example to demonstrate the formation of the magnesium salt of N,N-di-2-ethylhexyl dithiocarbamyl acetic acid.

EXAMPLE 1

One mol of KOH in the water solution was added to 1 mol of CS_2 while the temperature was maintained at 18–20° C. One mole of di-2-ethylhexyl amine was added to this drop-wise while maintaining the temperature at 18–20° C. After all the amine was added, the reaction product was allowed to warm to room temperature while stirring continuously. Water and excess CS_2 were removed by vacuum means leaving a heavy viscous amber liquid which was potassium N,N-di-2-ethylhexyl dithiocarbamate.

One mol of bromoacetic acid was dissolved in 200 ml. of ethanol. Ten drops of phenolphthalein was added to this and thereafter, KOH which had previously been dissolved in ethanol was added drop by drop to the bromoacetic acid solution until the first faint pink color was obtained designating the formation of potassium bromoacetate.

One mol of the previously formed potassium N,N-di-2-ethylhexyl dithiocarbamate was mixed with ethanol to form a solution and potassium bromoacetate was added slowly thereto. This was stirred for 5 hours at room temperature, acidified with HCl, water added and then extracted with ether. The extract was water-washed until free from acid, the ether was evaporated, benzene added and the washings were dried under reflux. The benzene was stripped off under reduced pressure and N,N-di-2-ethylhexyl dithiocarbamyl acetic acid was obtained as a dark amber red clear liquid. This was dissolved in dry toluene and warmed to 40–50° C. Magnesium methylate in an amount sufficient to react with the entire amount of the N,N-di-2-ethylhexyl dithio-

carbamyl acetic acid was added slowly. The product was heated to reflux and the methanol formed in the reaction removed. The solvent was stripped off under reduced pressure and 245 g. of 300 Pale Oil was added. This was then stripped for about 2 hours on a vacuum pump at 110° C. The resulting product is magnesium N,N-di-2-ethylhexyl dithiocarbamyl acetate.

Lubricating oils used in the instant invention are mineral lubricating oils of the naphthene distillate, paraffin distillate, mixed paraffin and naphthene distillate type and residual oils having a viscosity range from about 70 to 1400 SSU at 100° F. The preferred lube oils are furfural refined, solvent dewaxed paraffin base distillates having a viscosity of 540–600 SSU at 100° F.

The following table shows the results of bench tests using a base oil which was a furfural refined, solvent dewaxed, paraffin base distillate type mineral oil having a viscosity of 560 SSU at 100° F.; a flash of 465° F.; a pour of +5° F. and a V. I. of 92, and having 1% by weight of magnesium di-2-ethylhexyl dithiocarbamyl acetate incorporated therein.

Table 1

	1% Additive in Base Oil	Base Oil
MacCoull Corrosion Test:		
10 hr. Bearing Wt. Loss	32–28	110–118
Neut. No	3.6–3.8	14.0–14.3
MacCoull-Scholp Corrosion Test:		
10 hr. Bearing Wt. Loss	106–81	174–163
Neut. No	11.2–11.3	13.4–12.7
Beacon-Penn State Oxidation Test:		
Varnish, mg	5.7–2.7	10.8
Millimoles O_2 abs	24.2–24.9	20.9
Neut. No	2.7–2.8	3.8
Toetteher Varnish Test:		
Varnish, mg	0.5–0.3	14.8–15.6
Neut. No	14.0–14.1	6.1–5.9

The above tests are either well known or modifications of well known bench tests designed to preview characteristics of lubricant additives prior to engine testing. The MacCoull-Scholp corrosion test is similar to the well known MacCoull corrosion test and is further described in U. S. Patent 2,674,577 to Frederic C. McCoy, Bill L. Benge, Edwin C. Knowles and Chas. C. Towne, issued April 6, 1954. The Beacon-Penn. State oxidation test is a simplified small scale Penn. State oxidation test which has been primarily achieved by combining the ballast reservoir and oxygen burette into one vessel. The upper half of the vessel serves as the ballast reservoir, and the lower half as the calibrated burette. The change facilitated the design of a more compact unit and eliminated the pressure and temperature controls for one chamber. Except for some other minor modifications in design, the other basic features of the small scale Penn. State oxidation test are maintained.

We have subjected the additives of the instant invention to a Lauson L–4 engine test, the results of which follow. This test was performed on a blend of 50% by weight of a furfural refined, solvent dewaxed, paraffin base distillate type oil having an SSU viscosity of 153 at 100° F.; a flash of 400° F.; a pour of −10° F. and a V. I. of 98.5, and 47.5% of an airplane engine oil comprising a highly refined residuum from paraffin base crude oil, having an SUS viscosity of 1693 at 100° F.; a flash of 555° F.; a pour of +15° F. and a V. I. of 96.2. The blend had 2.5% of magnesium N,N-di-2-ethylhexyl dithiocarbamyl acetate incorporated therein.

Table 2

	2.5% Additive + Base Oil	Base Oil
Lauson L-4 Test: Bearing Wt. Loss, mg.	57	892-383

We have also tested the effectiveness of the combination of a salt of dialiphatic dithiocarbamyl aliphatic carboxylic acid and a detergent. The following table shows the result of a motor test with a mixture of 2 parts of the magnesium salt of N,N-di-2-ethylhexyl dithiocarbamyl acetic acid and 1 part zinc alkyl salicylate, wherein the alkyl group comprises olefin polymers having an average of 25 carbon atoms, incorporated in the previously disclosed preferred type oil used in the bench tests. 1.5% by weight of the combination was added to the base oil.

Table 3

	1.5% Additive + Base Oil	Base Oil
Lauson L-4 Test:		
Bearing Wt. Loss, mg.	138	333-380
Piston Rating	8.3	7.0

The results shown in the foregoing tables thoroughly demonstrate the effectiveness of our invention as a multifunctional additive for lube oils either utilizing the salt of aliphatic dithiocarbamyl aliphatic carboxylic acid alone or in combination with a detergent.

Obviously, many modifications and variations of the invention, as hereinbefore 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 proportion of a mineral lubricating oil and between 1 and 2 percent by weight of a mixture of about 2 parts of the magnesium salt of N,N-1-dialkyl dithiocarbamyl acetic acid wherein said alkyl group has from 4 to 12 carbon atoms, and about 1 part of zinc alkyl salicylate wherein said alkyl group has an average of from 20 to 30 carbon atoms.

2. A lubricant composition comprising a major proportion of a mineral lubricating oil and about 1.5 percent by weight of a mixture of about 2 parts of the magnesium salt of N,N-di-2-ethylhexyl dithiocarbamyl acetic acid and one part of zinc alkyl salicylate wherein said alkyl group has an average of 25 carbon atoms.

References Cited in the file of this patent

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U. S. DEPARTMENT OF COMMERCE

PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,832,737 James R. Roach et al. April 29, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 48, for "magnesium salt of N,N-1-dialkyl dithiocarbamyl acetic" read -- magnesium salt of N,N-dialkyl dithiocarbamyl acetic --.

Signed and sealed this 17th day of June 1958.

(SEAL)
Attest:
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