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LUBRICANTS CONTAINING METAL SALTS OF FATTY ACID DERIVATIVES OF DITHIOCARBAMIC ACID

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This invention relates to novel derivatives of dithiocarbamic acid and to the method of preparing same; more particularly it relates to the use of such novel compounds as improved corrosion inhibiting additives for lubricating oils.

The novel compounds of the present invention have particular utility for inhibiting the corrosion of bearing surfaces in internal combustion engines, particularly alloy bearings such as copper-lead, cadmium-nickel, cadmium-silver, etc., as well as pure silver bearings. Bearings comprising such metals have definite well-known mechanical advantages in internal combustion engines, but under the high temperatures and heavy loads of modern high speed operating conditions they appear to promote oxidation of highly refined lubricating oils, resulting in varnish and sludge formation, ring and valve sticking and excessively high bearing losses which have heretofore been attributed largely to corrosion by acids produced by the oxidation of the oil. In addition, it has been found that additives which have been placed in lubricating oils to inhibit the formation of sludge, varnish, etc., e. g. neutralized reaction products of a phosphorus sulfide and an olefin or olefin polymer, have aggravated this corrosion problem.

The art has taught the addition of certain dithiocarbamic acid derivatives, e. g. the salts and esters thereof, to mineral lubricating oils for the purpose of inhibiting corrosion of bearings of the type herein referred to. Although the addition of such dithiocarbamo derivatives has resulted in mineral lubricating oils which exhibit substantially reduced corrosiveness, an attendant problem has arisen which is equally serious and for which a solution has thus far not been forthcoming. This problem, viz. vastly increased bearing wear, has now been traced to the thiocarbamic acid derivatives heretofor employed. A new class of metal salts of fatty acid derivatives of dithiocarbamic acid has now been discovered, the members of which are particularly effective corrosion inhibitors in mineral lubricating oils in contact with bearings of the type described, and which at the same time cause substantially less wear of the bearing surfaces as compared to related compounds heretofore employed in the art.

Since certain known thiocarbamic acid derivatives have exhibited satisfactory corrosion inhibiting properties when added to a lubricating oil, it is an object of this invention to retain the advantages thereof while substantially reducing their wear producing properties. It is a further object to provide a novel class of metal salts of thiocarbamo derivatives which are effective in inhibiting corrosion of bearing surfaces by mineral lubricating oils without resulting in greatly increased wear of such surfaces. Other objects will become apparent from the ensuing description hereof.

The novel class of dithiocarbamic acid derivatives has the following general formula:

$$[RR'NCSYCOO]_xM$$
$$\|$$
$$S$$

wherein R and R' may be hydrogen or a hydrocarbon radical, e. g. alkyl, aryl, cycloalkyl, arylalkyl or alkylaryl radicals containing from one to about twenty carbon atoms; Y represents an acyclic hydrocarbon radical containing from one to about twenty carbon atoms; M is a polyvalent metal, preferably selected from group II of the periodic table; the total number of carbon

atoms in R, R', and Y should be at least about nine and preferably at least about 12 to impart substantial oil solubility to the compounds when they are employed as corrosion inhibiting additives in lubricating oils; and x is a positive integer equal to the valence of M. Such compounds may be prepared by reacting the alkali metal salt of a dithiocarbamic acid with an alkali metal salt of a halogenated fatty acid, followed by decomposition of the resulting alkali metal salt of the dithiocarbamo substituted fatty acid with a water or alcohol soluble salt of a metal of the class indicated.

Dithiocarbamic acid salts from which the compounds of the present invention are derived may be readily prepared by reacting carbon disulfide with ammonia or a primary or secondary amine in the presence of alkali. These salts may then be reacted with the alkali salt of a halo substituted fatty acid to produce the alkali salt of a fatty acid substituted dithiocarbamic acid which in turn may be reacted with a salt of a polyvalent metal which is soluble in water or alcohol to produce compounds of the present invention. The following equations illustrate these reactions:

(1) $$RR'NH_2 + CS_2 + NaOH \longrightarrow RR'NCSNa + H_2O$$
$$\|$$
$$S$$

(2)
$$RR'NCSNa + XYCOONa \longrightarrow RR'NCSYCOONa + NaX$$
$$\|\qquad\qquad\qquad\qquad\qquad\|$$
$$S\qquad\qquad\qquad\qquad\quad S$$

(3)
$$xRR'NCSYCOONa + MZx \longrightarrow [RR'NCSYCOO]_xM + xNaZ$$
$$\|\qquad\qquad\qquad\qquad\quad\|$$
$$S\qquad\qquad\qquad\qquad S$$

In the above equation R, R', Y, and M represent the same constituents as hereinabove indicated; X represents a halogen; Z represents a monovalent anion, e. g. a halogen, which in combination with the metal of the class defined affords a water or alcohol soluble salt; and x represents a positive integer equal to the valence of M.

Examples of compounds of the above designated class which are particularly suitable for use as lubricant additives in accordance herewith may be mentioned the polyvalent metal salts of dibutyl dithiocarbamo stearic acid, ethyl hexyl dithiocarbamo lauric acid, dithiocarbamo stearic acid, butyl dithiocarbamo stearic acid, etc. Preferred examples of polyvalent metals which may be used in accordance herewith are zinc, barium, calcium, strontium, magnesium, and aluminum.

The amines employed in the initial reaction (Equation 1 above) may be primary or secondary, depending upon whether or not either R or R' is a hydrogen atom and they may contain from 1 to about 20 carbon atoms. Thus, such amines as methylamine, ethylamine, butylamine, nonylamine, stearylamine, cyclohexylamine, phenylamine, diethylamine, diisopropylamine, dibutylamine, ethyl hexylamine, lauryl hexylamine, etc. may be employed in accordance herewith. Potassium hydroxide may be employed instead of sodium hydroxide if desired.

As examples of typical carboxylic acids, the alkali salts of which are employed in accordance with Equation 2 above, may be mentioned the halo-derivatives of acetic acid, propionic acid, butyric acid, hexanoic acid, nonanoic (pelargonic) acid, lauric acid, oleic acid, stearic acid, caprylic acid, isovaleric acid, isocaproic acid, etc. The most readily prepared, generally available, and preferred halo-acids are those with the halogen in the alpha (α) position, and of these the chloro-derivatives are preferred for use in accordance herewith but in the higher molecular weight ranges the bromo-derivatives are more readily available and entirely suitable.

It should be understood that the suggestions of various specific compounds for use in accordance herewith is not intended to function expressly or impliedly for the exclusion of others falling within the defined classes but which may not be specifically set forth herein.

The preparation of the halogenated carboxylic acids and alkali salts thereof which are employed in accordance herewith do not constitute a feature of the present invention and consequently will not be described in great

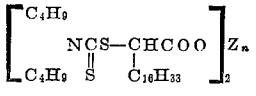
detail. They may be prepared, for example, by brominating or chlorinating a carboxylic acid with bromine in the presence of red phosphorous, PCl_3, etc., or by any other known method. Reference is made to "Organic Preparations" by C. Weygand (Interscience Publishers, Inc., N. Y., 1945) page 79 et seq. wherein methods for the chlorination and bromination of carboxylic acids are described.

The reaction of the alkali salt of a halogenated carboxylic acid and the alkali salt of a dithiocarbamic acid derivative may be carried out at a temperature in the range of from about 25° to about 200° C. in from about 1 to about 6 hours. It is preferred, however, to react these materials at a temperature in the range of from about 50° to about 100° C.; the reaction is usually completed in about 2 to about 4 hours at such temperature with the higher molecular weight carboxylic acids taking the longer periods. The carboxylic acid salt is preferably added to the dithiocarbamic acid derivative in an aqueous alcoholic solution; ethanol or methanol, for example, may be used for the purpose.

The method in which the novel compounds of the present invention are prepared may be better understood by reference to the following illustrative examples.

EXAMPLE 1

One mole of CS_2 was slowly added to a well-stirred mixture consisting of one mole of di-n-butyl amine and a 25% aqueous solution of one mole of NaOH. After addition of CS_2 was completed an aqueous solution containing 25% ethanol and one mole of sodium α-bromostearate was added while stirring continuously. The temperature was raised to about 50° C. during the addition of the latter reactant and maintained there for about one hour. The resulting sodium salt of di-n-butyldithiocarbamo stearic acid was methathesized with one equivalent of zinc chloride to yield a product which analyzed 12.0% sulfur, 2.6% nitrogen, and 5.95% zinc as compared to calculated values of 12.3%, 2.7% and 6.3% respectively for



EXAMPLE 2

One mole of CS_2 was slowly added to a well-stirred mixture consisting of one mole of di-n-butylamine and a 25% aqueous solution of one mole of NaOH. Upon completion of CS_2 addition (about one hour), the reaction mixture was stirred for an additional hour and there was then added a 25% aqueous solution of one mole of sodium β-chloropropionate. The mixture was then stirred at a temperature of 50° to 60° C. for another hour after which a 50% aqueous solution of 0.5 mole of $ZnCl_2$ was added and a light brown viscous liquid was produced in 93% yield which had a sulfur analysis of 18.4%, a nitrogen analysis of 4.14% and contained 9.99% zinc. Based upon this analysis, the product was zinc β (n-dibutyl dithiocarbamo) propionate for which the calculated values are 20.7%, 4.54%, and 10.52% respectively.

EXAMPLE 3

The sodium salt of dibutyl dithiocarbamic acid was prepared in accordance with the same technique as set forth in the above examples and to this product was added an aqueous solution containing 25% ethanol and one mole of sodium α bromododecanoate. This mixture was then stirred for an hour at a temperature of from about 60° to 70° C., after which the addition of a 50% aqueous solution of 0.5 mole of $ZnCl_2$ resulted in a production of a brown viscous liquid in 96% yield. This material analyzed 13.8% sulfur, 2.89% nitrogen and 7.42% zinc as compared to calculated values of 14.73%, 3.22% and 7.48% respectively for zinc α (n-dibutyl dithiocarbamo) dodecanoate.

EXAMPLE 4

The sodium dibutyl dithiocarbamic acid salt was prepared in accordance with the method of Example 1 and

reacted with sodium α bromododecenoate in a manner similar to that set forth in Example 3. The resulting product was then heated for about an hour at a temperature of from 60° to 70° C. and a 50% aqueous solution of 0.5 mole of $BaCl_2$ was added to produce a product in 90% yield which analyzed 13.3% sulfur, 2.65% nitrogen and 14.49% barium. This established the preparation of the product barium α (n-dibutyl dithiocarbamo) dodecanoate for which the calculated analysis of sulfur, nitrogen and barium are 13.6%, 2.97% and 14.55% respectively.

EXAMPLE 5

The sodium dibutyl dithiocarbamate was produced in accordance with the method of Example 1 and reacted with a 25% aqueous solution of sodium α chloroacetate by mixing the same and heating to a temperature of from about 50° to 60° C. for about one hour. At the end of that period, a 50% aqueous solution of 0.5 mole of $ZnCl_2$ was added thereto to produce, in 88% yield, a product which analyzed 20.2% sulfur, 4.46% nitrogen and 10.2% zinc. Thus the product was zinc (α n-dibutyl dithiocarbamo) acetate for which the calculated values of sulfur, nitrogen and zinc are 21.7%, 4.7% and 11.0% respectively.

EXAMPLE 6

About one-half mole of CS_2 was added slowly (about ½ hour) to a well-stirred mixture consisting of 0.5 mole of Armeen 2C (a product of Armour and Company comprising 80% secondary amines consisting of 8% di-C_8amine, 9% di-C_{10}amine, 47% di-C_{12}amine, 18% di-C_{14}amine, 8% di-C_{16}amine and 10% di-C_{18}amine and having an approximate molar combining weight of 435) and 0.5 mole of KOH in 75 cc. of water and 200 cc. of ethanol. After addition was complete the temperature had risen to 34° C. and was then heated to 46° C. for another 25 minutes after which the organic layer was added to 0.5 mole of the potassium salt of α bromolauric acid in 300 cc. of water and heated with stirring to 55° C. for one hour. About .3 mole of $ZNCl_2$ in 75 cc. of water was added and heated to 55° C. for 1½ hours after which hexane was added to obtain separation and after washing several times with water and filtering, a product analyzing 5.25% zinc, 7.86 sulfur and 2.12 nitrogen was obtained.

The effectiveness of compounds of the above type as improved corrosion inhibitors is demonstrated by the data set forth in the table consisting of the results of certain tests, the conditions of which are considered to be more severe than in the actual operation of an internal combustion engine.

The percentages of additive employed in the examples set forth in the table are based upon substantially equivalent sulfur contents; thus, with higher molecular weight additives larger amounts are required. The reduction in corrosion of the base oil containing a detergent additive when a dithiocarbamo-compound (either of the present invention or of the prior art) is used is striking. The wear increase caused by the introduction of the prior art corrosion inhibiting additive (zinc ethyl hexyl dithiocarbomate), however, is exceedingly great whereas the use of the zinc acetate derivative of dibutyl dithiocarbamic acid, which contains the minimum of ten carbon atoms and does increase wear slightly as compared to the base oil, results in about 62% less wear for the solvent extracted oil which is free of detergent additive and in a 96% improvement for an oil containing such a detergent additive. The higher molecular weight stearic acid derivative of dithiocarbamic acid provides a substantial improvement in wear as compared to the base oil, with or without a detergent additive. The corrosion data is lacking in Examples III, V and VII of the table because all tests in this series wherein a dithiocarbamo compound was added were conducted with detergent additive containing oils. From other tests, however, it is certain that the reduction in corrosion resulting from addition of a dithiocarbamo compound to straight base oil is at least as great as shown for the oil plus detergent additive. In this regard it should be noted that the corrosion caused by an oil without a detergent additive is only about one-half that of the oil plus detergent additive before any corrosion inhibitor is added.

Table

Lubricant	Corrosion Test (S. S. C. T.)[3]	Wear Test (Modified Shell-4 Ball Test)[4]
I—Solvent Extracted 30 Base oil = (A)	585	0.87
II—Sol. Extr. 30 Base oil + 1.65% detergent additive[1] = (B)	1,131	0.89
III—(A) + 0.75% zinc ethylhexyl dithiocarbamate[2]		2.18
IV—(B) + 0.75% zinc ethylhexyl dithiocarbamate[2]	25	1.98
V—(A) + 1.05% zinc (n-dibutyl dithiocarbamo) acetate		1.34
VI—(B) + 1.05% zinc (n-dibutyl dithiocarbamo) acetate	34	1.01
VII—(A) + 1.80% zinc (n-dibutyl dithiocarbamo) stearate		0.78
VIII—(B) + 1.80% zinc (n-dibutyl dithiocarbamo) stearate	30	0.78

[1] KOH neutralized reaction product of P_2S_5 and butylene polymer diluted with 40% mineral oil.

[2] Typical prior art additive having excellent corrosion inhibiting properties.

[3] Cu-Pb bearings are immersed in a beaker of the oil containing 50 g. of sand (30-35 mesh) and 0.25% PbO. The oil is stirred at 300° F. and the bearings are weighed at 24, 48 and 72 hours.

[4] The Shell Four Ball Test was modified by replacing the stationary three ball platform with an insert containing three silver disks. Test conditions—600 R. P. M., 7 kgs. load, 105° C. and ½ hr.

The novel compounds of the present invention may be employed in natural or synthetic lubricating oils but they have particular use in solvent extracted mineral lubricating oils since it is with such oils that the problems of corrosion are the greatest. Thus, it has been found that solvent extracted lubricating oils cause corrosion to alloy bearings of the cadmium-silver type to the extent of 5 mg./cm.^{2} and even greater when such bearings are submerged for 25 hours or less in an air agitated oil which has been preoxidized at about 340° F. for 25 to 50 hours.

It has been found that corrosiveness is inhibited and that highly desirable properties are imparted to lubricating oils by adding thereto an amount of about 0.005% up to about 5%, and preferably from about 0.1% to about 3% of compounds of the type hereinabove described. The addition to lubricating oils of even greater amounts, up to about 10%, is contemplated for the purpose of improving film strength thereof and imparting extreme pressure characteristics and lubricity.

The term "neutralized phosphorous sulfide-olefin reaction product" as used herein means a phosphorous sulfide-olefin reaction product having at least about 1% of its titratable acidity reduced by the reaction with a basic reagent, and includes the neutralized phosphorous sulfide-olefin reaction product containing a metal constituent resulting from said neutralization or resulting from the reaction of a heavy metal salt of the phosphorous sulfide-olefin reaction product with a basic reagent. For a more detailed description of such reaction product and the method of preparing same, reference is made to U. S. 2,316,090.

In accordance with the present invention the foregoing neutralized reaction product may be employed in lubricants in amounts within the range of from about 0.001% to about 10% and preferably from about 0.01% to about 3%. These reaction products are extremely viscous and it is ordinarily desirable to dilute same with a suitable hydrocarbon oil in order to promote their addition to

lubricating oil, as indicated in the table. In accordance herewith, however, in the appended claims the percentages of such neutralized phosphorous sulfide-olefin reaction products which are given are on the basis of the undiluted reaction product.

Having thus described my invention what I claim as novel and desire to protect by Letters Patent is as follows:

1. A lubricant composition comprising a mineral lubricating oil and from 0.005% to 10% by weight of a component having the general formula

$$[RR'NCSYCOO]_xM$$
$$\|$$
$$S$$

wherein R and R' are constituents selected from the group consisting of hydrogen and a hydrocarbon radical, Y is an acyclic hydrocarbon radical containing from 1 to about 20 carbon atoms, M is a polyvalent metal, x is a positive integer equal to the valence of M and the total of the number of carbon atoms in R, R' and Y is at least 9.

2. The lubricant composition of claim 1 wherein, in the component defined is terms of the general formula, R and R' are alkyl radicals, x is 2 and M is selected from group II of the periodic table.

3. The lubricant composition of claim 1 wherein, in the component defined in terms of the general formula, R and R' are n-butyl radicals, x is 2 and M is selected from group II of the periodic table.

4. The lubricant composition of claim 1 wherein, in the component defined in terms of the general formula, R and R' are n-butyl radicals, x is 2 and M is zinc.

5. The lubricant composition of claim 1 wherein, in the component defined in terms of the general formula, R and R' are n-butyl radicals, x is 2 and M is barium.

6. A lubricant composition comprising a mineral lubricating oil, from 0.005% to 10% by weight of a component having the general formula

$$[RR'NCSYCOO]_xM$$
$$\|$$
$$S$$

wherein R and R' are constituents selected from the group consisting of hydrogen and a hydrocarbon radical, Y is an acyclic hydrocarbon radical containing from 1 to about 20 carbon atoms, M is a polyvalent metal, x is a positive integer equal to the valence of M and the total of the number of carbon atoms in R, R' and Y is at least 9, and from 0.001% to about 3% of a neutralized phosphorus sulfide-olefin polymer reaction product.

7. A lubricant composition comprising a mineral lubricating oil and from 0.005% to 10% by weight of zinc α(di-n-butyldithiocarbamo) stearate.

8. The lubricant composition of claim 7 which contains from about 0.001% to about 10% of a neutralized phosphorus sulfide-olefin polymer reaction product.

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