Patented Mar. 30, 1954

2,673,839

UNITED STATES PATENT OFFICE

2,673,839

LUBRICATING OIL COMPOSITION

Abraham D. Kirshenbaum, Philadelphia, Pa., and James M. Boyle, Bayonne, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application April 28, 1951, Serial No. 223,658

21 Claims. (Cl. 252—47.5)

1

The present invention relates to the improvement of lubricants and lubricating oil compositions and is concerned chiefly with the preparation of improved lubricants by incorporating therein a new class of additives which impart improved properties to the composition. More specifically, it has been found that the condensation product of a thiocarbamic acid and a sulfide of a halogen substituted fatty acid halide and a carboxylic ester is an effective additive material for lubricants having corrosion inhibition, detergency and extreme pressure properties.

As is well known in the art, many lubricating oils such as the petroleum base lubricants are not always resistant to oxidation under severe service conditions and soluble acidic oxidation products which are corrosive to metallic parts are frequently formed. The tendency to form corrosive bodies may be particularly serious in certain of the highly refined lubricants. Some oils also deposit films of varnish on hot metal surfaces, such as the pistons of internal combustion engines, under severe engine operating conditions.

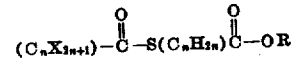
It is also well known that many ordinary mineral base lubricants and greases employed under extremely heavy load conditions may fail causing the metal surfaces to contact each other directly. Under such conditions high temperatures are generated which result in seizure or excessive wear of the metal parts. Mineral oils compounded with modifiers including elements such as sulfur, chlorine and phosphorus tend to impart desirable properties to the oils. Apparently, these elements react with the metal surfaces at high temperatures and form a protective film which tends to avoid direct contact and seizure of the metal parts.

In accordance with the present invention, a new class of compounds has been discovered which substantially reduces the tendency of oils to corrode metal surfaces. The compounds are also effective in dispersing sludge and maintaining a clean engine condition when the oil is employed as a crankcase lubricant. In addition the compounds of the present invention, which are derived from a parent material known to have desirable extreme pressure properties but which is under some conditions corrosive to the metal parts, maintain certain desirable characteristics

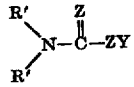
2

of the parent compound and yet act as corrosion inhibitors.

The additives of the present invention are condensation products of a thiocarbamic acid or salt thereof and a sulfide of a halogen-substituted, low molecular weight, saturated fatty acid halide and a carboxylic ester. Specifically, a compound having the following formula—

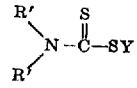


wherein X is an element selected from the class consisting of the halogens and hydrogen and at least one X is a halogen, n is an integer from 1 to 4, and R is a hydrocarbon radical, is condensed with at least one thiocarbamic acid having the following formula—

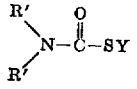


wherein R′ is selected from the class consisting of hydrogen and hydrocarbon radicals, Z is selected from the class consisting of sulfur and oxygen and at least one Z is sulfur, and Y is selected from the class consisting of hydrogen and a metal equivalent thereof. The reaction is carried out such that at least one halogen atom in the C_nX_{2n+1} radical is replaced by a thiocarbamate radical. The hydrocarbon radicals, R and R′ promote the solubility of the product in oil. They may be alkyl radicals such as the straight or branched chain radicals and may be saturated or unsaturated. The alkyl radicals generally include methyl, ethyl, propyl, butyl, isobutyl, isopentyl, octyl, and higher molecular weight radicals. They may also be aryl, aralkyl or alkaryl radicals. Suitable aryl groups include phenyl and naphthyl; the benzyl group is representative of the aralkyl radical. The alkaryl radicals include those corresponding to toluene, isopropyl-benzene, tertiary amyl benzene, octyl benzene, and the like. R preferably has from 1 to 14 carbon atoms whereas R′, when a hydrocarbon radical rather than hydrogen, preferably has from 1 to 8 carbon atoms. Preferably, at least one of the R′ is a hydrocarbon radical.

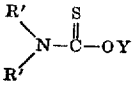
The thiocarbamic acids that may be used in the practice of the present invention follow:



Dithiocarbamic acid or salt



Thiolcarbamic acid or salt



Thionocarbamic acid or salt

When Y is a metal equivalent of hydrogen, the reactive alkali and alkaline earth metals such as sodium, potassium and the like are preferably employed. The dithiocarbamic acid is generally preferred in producing the product.

The sulfide complex employed in preparing the additive may be made by reacting a halogen substituted saturated fatty acid halide with a mercapto carboxylic ester or a metal salt thereof.

The halogens substituted on the alkyl radical of the fatty acid halide may be chlorine, bromine, iodine and the like or mixtures of two or more halogens. Halogens in the alpha position with respect to the carbonyl group are more reactive than those in the beta and gamma positions; hence, the more reactive iodo and bromo rather than the less reactive chloro and fluoro compounds may be desired when the halo radical is not positioned on a carbon atom adjacent the activating carbonyl group. On the other hand, if the finished condensation product should retain chloro-, or less preferably bromo-, radicals in order to strengthen its extreme pressure properties, mixed halo substituents may be employed such that a more reactive halogen, such as iodine, will be preferentially replaced by a thiocarbamate radical leaving a less reactive halogen such as chlorine in the product. Such acid halides as monochloro acetyl halide; trichloro acetyl halide; alpha bromo propionyl halide; alpha, alpha-dichloro propionyl halide; alpha, alpha-dichloro, beta-bromo butyryl halide, and the like may be employed. Preferably the acid chlorides are used because of economic considerations, although the bromides and iodides may be used satisfactorily under certain conditions.

Mercapto carboxylic esters such as the esters of thioglycolic acid, alpha-mercapto propionic acid, alpha-mercapto butyric acid, alpha-mercapto isobutyric acid, and the like, and their metal salts may be used for reacting with the acid halide.

In preparing the sulfide, the acid halide may be added slowly to the mercapto carboxylic ester or to a solution of the latter in a relatively inert solvent such as benzene. Generally, approximately equimolar concentrations of the acid halide and mercaptol carboxylic ester are used in forming the sulfide.

The thiocarbamic acids and their salts may be prepared by known means. For example, sodium dithiocarbamate is readily prepared by slowly adding carbon disulfide to a mixture of alkali metal hydroxide and a primary or secondary amine in the presence of a suitable inert medium such as methyl ethyl ketone.

In the reaction of the thiocarbamate with the sulfide, one of the reactants is added relatively slowly to the other, cooling being employed if necessary to prevent excessive temperature rise as a result of the exothermic reaction which takes place. The reactants are then heated together for a period of from about 0.5 to 2 hours depending on the types of materials used and on the extent to which it is desired that the reaction proceed. Preferably, temperatures in the range of 0° C. to 150° C. are employed. Conveniently, the reaction may take place in the presence of a solvent such as ethyl alcohol, isopropyl alcohol, acetone, methyl ethyl ketone, dioxane, or the like. In this latter case, heating may be carried out under refluxing conditions. If a metal salt of a thiocarbamic acid is used, a substantially inert solvent should be employed in which the resulting metal halide is insoluble and will precipitate out of solution. The metal halide may then be removed by filtration, decantation, or other means. If a thiocarbamic acid is used as a reactant, any hydrogen halide remaining in solution should be neutralized to form an insoluble salt or otherwise removed from the reaction product. Solvent may be removed from the product by stripping with nitrogen or other inert gas, by distillation or by other means.

If the finished product is to be substantially free of halogen, at least one mol of thiocarbamic acid should be employed for each atom of halogen in the sulfide. In any event, equimolar proportions of the thiocarbamic acid and sulfide will generally be used. If it is preferred that the finished condensation product retain chlorine or bromine molecules to strengthen its extreme pressure properties, controlled quantities of the thiocarbamates will be added to replace only a portion of the halogen atoms. It will be recognized in this latter case that the partial substitution of the halogens with the thiocarbamates not only improves the detergency and corrosion inhibition properties of the finished product but also permits the product to retain the desirable extreme pressure properties to a greater extent than is the case when all halogens are removed.

If the products of the present invention are added to mineral oil for the purpose of inhibiting oxidation and for dispensing sludge, they are preferably added in proportions of 0.01 to 5%, more preferably from about 0.1 to 2% by weight. The proportions giving the best results in any given case will vary somewhat according to the nature of the additive and of the base oil and in accordance with the specific purpose for which the oil is to be used. It is quite convenient, when employing the additive commercially, to prepare a concentrated lubricating oil solution in which the amount of the additive in the composition ranges from 25 to 50% by weight and to transport and store in such form. Thus, in preparing a finished lubricating oil composition, such as for use in the crankcase of an internal combustion engine, the additive concentrate may be blended with the base oil in the required amount. If, on the other hand, the additive material is to be used as an extreme pressure additive, somewhat higher concentrations, in the order of from 5 to 20% based on the finished composition, will generally be employed.

The invention will be more fully understood by reference to the following examples. It is pointed out, however, that the examples are given for the purpose of illustration only and are not to be construed as limiting the scope of the present invention in any way.

Example 1

(*a*) 12 g. (0.3 mol) of sodium hydroxide flakes and 100 cc. of methyl ethyl ketone were placed in a 500 cc. reaction flask. 22 g. (0.3 mol) of normal butyl amine were added to the flask and the solution was cooled in an ice bath. 23 g. (0.3 mol) of carbon disulfide dissolved in 100 cc. of methyl ethyl ketone were added dropwise with continual stirring to the solution and after addition of the disulfide had been completed, the solution was stirred at room temperature for about 1 hour.

(*b*) 27 g. (0.1 mol) of trichloroacetyl ethyl acetate sulfide (prepared by reacting trichloroacetyl chloride and ethyl thioglycolate) was added cautiously to the solution prepared as in (*a*) which contained approximately 0.3 mol of sodium n-butyl thiocarbamate. Heat was evolved from the exothermic reaction that took place; however, the reaction was easily controlled. The reaction solution was heated for 1 hour at the refluxing temperature of methyl ethyl ketone and the product was then filtered through a diatomaceous filter aid ("Hyflo") to remove precipitated sodium chloride. The material was then blown with nitrogen on a steam bath to remove the solvent. The condensation product, believed to be substantially

$$(C_4H_9NH\text{–}CS\text{–}S)_3C\text{–}CO\text{–}S\text{–}CH_2\text{–}CO\text{–}O\text{–}C_2H_5$$

was found to have 6.94% nitrogen and 0.55% chlorine. It is therefore indicated that the chlorine in the trichloroacetyl ethyl acetate sulfide was almost completely replaced by the butyl thiocarbamate radical.

Example 2.—Lauson engine test

The product prepared as described in Example 1 (*b*) was tested in a Lauson engine using a blend of 1.0% by weight of the product in a solvent extracted Coastal naphthenic oil of 60 seconds viscosity (Saybolt) at 210° F. A sample of the unblended base oil was also tested for comparison purposes. The test was conducted for a period of 25 hours, the Lauson engine being operated at 1800 R. P. M. with a 1.5 indicated kilowatt load, 300° F. oil temperature and 295° F. water jacket temperature. The oils were then rated on a demerit system wherein a perfectly clean surface is given a rating of 0, while a rating of 10 is given the worst condition that can be expected of that surface. Observations were also made on the loss in weight of the copper-lead bearings during the test. The results are shown in the following table.

Lubricant	Piston Varnish Demerit	Cu-Pb Bearing Weight Loss Gm./Bearing)
Unblended base oil	6.25	0.080
Base oil + 1% product of Example 1(*b*)	3.25	0.008

It is thus seen that the condensation product has desirable detergency characteristics and very excellent corrosion inhibiting properties.

Example 3.—Laboratory bearing corrosion test

A blend was prepared containing 0.25% by weight of the additive prepared as described in Example 1 (*b*) using as the base oil a solvent extracted, paraffinic type mineral lubricating oil of SAE–20 viscosity grade. A sample of this blend and a sample of the unblended base oil were submitted to a laboratory test known as the S. O. D. Corrosion Test, designed to measure the effectiveness of the additive in inhibiting the corrosiveness of a typical mineral lubricating oil towards the surfaces of copper-lead bearings. The test was conducted as follows:

500 cc. of the oil was placed in a glass oxidation tube (13 inches long and 2⅝ inches in diameter) fitted at the bottom with a ¼ inch air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each four-hour period the bearings were removed, washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional four-hour periods in like manner. The results are given in the following table as "corrosion life," which indicates the number of hours required for the bearings to lose 100 mg. in weight, determined by interpolation of the data obtained in the various periods.

Oil	Bearing Corrosion Life (Hrs.)
Unblended base oil	10
Base oil + 0.25% product of Example 1(*b*)	25

It is also noted from the results of this test that the additive was effective as a corrosion inhibitor. These data are interesting in view of the fact that the parent compound, trichloroacetyl ethyl acetate sulfide, used in making the product, is an excellent extreme pressure additive but is corrosive to metals under some conditions. Modification of the molecule in accordance with the present invention, however, results in a product that inhibits corrosion.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, phosphites, thiophosphates and thiophosphites, metal xanthates and thioxanthates, metal thiocarbamates, and the like. Other types of additives, such as phenols and phenol sulfides, may also be present.

The lubricating oil base stock used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced by solvent extraction with solvents such as phenol, sulfur dioxide, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils resembling petroleum oils, prepared,

for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products.

For the best results the base stock chosen should normally be an oil which with the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils, no strict rule can be laid down for the choice of the base stock. The additives are normally sufficiently soluble in the base stock, but in some cases auxiliary solvent agents may be used. The lubricating oils will usually range from about 35 to 150 seconds (Saybolt) viscosity at 210° F. The viscosity index may range from 0 to 100 or even higher.

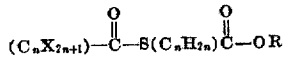
Other agents than those which have been mentioned may be present in the oil composition, such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, and the like.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8 to 20 carbon atoms, e. g., octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

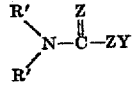
In addition to being employed in lubricants, the additives of the present invention may also be used in other mineral oil products such as motor fuels, heating oils, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils, process oils, and the like, and generally as anti-oxidants in mineral oil products. They may also be used in gear lubricants, greases and other products containing mineral oils as ingredients.

What is claimed is:

1. As a new composition of matter, the product obtained by condensing a sulfide having the formula—



wherein n is from 1 to 4, X represents an element selected from the class consisting of the halogens and hydrogen and at least one X is a halogen, and R is a hydrocarbon radical, with a thiocarbamic acid having the following formula—



wherein R′ is selected from the class consisting of hydrogen and hydrocarbon radicals, Z is selected from the class consisting of sulfur and oxygen and at least one Z is sulfur, and Y is selected from the group consisting of hydrogen and a metal equivalent thereof.

2. A composition as in claim 1 wherein the thiocarbamic acid is a dithiocarbamic acid.

3. A composition as in claim 1 wherein the thiocarbamic acid is a thiolcarbamic acid.

4. A composition as in claim 1 wherein the thiocarbamic acid is a thionocarbamic acid.

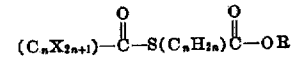
5. A composition as in claim 1 wherein (C_nX_{2n+1})— is a CCl_3— radical.

6. A composition as in claim 1 wherein at least one mol of said thiocarbamic acid is reacted with each mol of said sulfide.

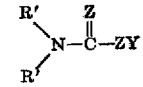
7. A composition as in claim 1 wherein R has from 1 to 14 carbon atoms.

8. A composition as in claim 1 wherein at least one R′ is a hydrocarbon radical having from 1 to 8 carbon atoms.

9. A composition consisting essentially of a mineral oil and a minor proportion of the condensation product obtained by reacting a sulfide having the following formula—



wherein n is from 1 to 4, X represents an element selected from the class consisting of the halogens and hydrogen and at least one X is a halogen, and R is a hydrocarbon radical, with a thiocarbamic acid having the following formula—



wherein R′ is selected from the class consisting of hydrogen and hydrocarbon radicals, Z is selected from the class consisting of sulfur and oxygen and at least one Z is sulfur, and Y is selected from the group consisting of hydrogen and a metal equivalent thereof.

10. A composition as in claim 9 wherein said mineral oil is a lubricant base stock and said minor amount is in the range of 0.01 to 20% by weight of said condensation product.

11. A composition as in claim 9 wherein said thiocarbamic acid is a dithiocarbamic acid.

12. A composition as in claim 9 wherein said thiocarbamic acid is a thiolcarbamic acid.

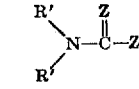
13. A composition as in claim 9 wherein said thiocarbamic acid is a thionocarbamic acid.

14. A composition as in claim 9 wherein R is an ethyl radical.

15. A composition as in claim 9 wherein at least one R′ is a butyl radical.

16. A composition consisting essentially of a mineral lubricating oil and in admixture therewith a minor proportion of the product obtained by condensing at a temperature in the range of 0° C. to 150° C. trichloroacetyl ethyl acetate sulfide with at least a molar equivalent of an alkali alkyl dithiocarbamate.

17. The method which comprises condensing a sulfide of a halogen substituted fatty acid halide having in the range of 1 to 5 carbon atoms and a carboxylic ester, and a thiocarbamic acid having the formula—



wherein R′ is selected from the class consisting of hydrogen and hydrocarbon radicals, Z is selected from the class consisting of sulfur and oxygen and at least one Z is sulfur, and Y is selected from the group consisting of hydrogen and a metal equivalent thereof to form a product and removing halide reaction products therefrom.

18. A method according to claim 17 in which said condensation is conducted in the presence of a substantially inert solvent.

19. A method according to claim 18 in which Y is a metal equivalent of hydrogen whereby a metal halide insoluble in said solvent is formed.

20. A method which comprises heating trichloroacetyl ethyl acetate sulfide and at least a molar equivalent of sodium butyl dithiocarbamate in the presence of methyl ethyl ke-

tone at the refluxing temperature of the latter for a period of about one hour, filtering to remove by-product sodium chloride, and removing said ketone from the resulting product.

21. As a new composition of matter, the reaction product of trichloroacetylethyl acetate sulfide and an alkali metal n-butyl dithiocarbamate.

ABRAHAM D. KIRSHENBAUM.
JAMES M. BOYLE.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,396,789	Hunt	Mar. 19, 1946
2,438,599	Blake	Mar. 30, 1948
2,491,772	Rudel	Dec. 20, 1949
2,510,773	Clinton	June 6, 1950
2,574,996	Allen et al.	Nov. 13, 1951