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ALIPHATIC TRITHIOCARBONATES

Darwin E. Badertscher and Charles F. Feasley, Woodbury, and Henry G. Berger, Glen Rock, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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4 Claims. (Cl. 260—455)

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This invention has to do with the treatment of hydrocarbon products such as mineral oils to improve their characteristics, and more specifically to the addition to petroleum lubricating oils of characterizing agents which improve their ability to resist the deteriorating effect of oxidation and their ability to lubricate bearing surfaces which are subjected to extreme pressures such as are now commonly encountered in hypoid gears and the like.

Moderately refined oils, such as motor oils and other moderately refined lubricating oils normally used under conditions of exposure to oxidation in the presence of metals, oxidize to sludge and/or acidic oxidation products normally corrosive to the metals which they encounter in use, as, for example, bearing metals in automotive use. It has now been found that stabilization of these oils against such oxidation effects may be conveniently accomplished by addition to the oils of certain materials which substantially retard the oxidation of the oils, whether or not metal is present, or by the addition of certain other materials which apparently have the ability to inhibit the catalytic effect of metals in promoting oxidation reactions and thus prevent the formation of sludge and/or acidic constituents and the like under normal conditions of use and achieve an equally good practical result, although materials of the latter class may be incapable of inhibiting oxidation of oils in the absence of metals. This invention has to do with stabilizing reaction products which appear to be of this latter class, not heretofore known to be effective for this purpose, and with oils stabilized by the use of these reaction products.

Recent changes in automotive engine design tending toward higher bearing pressures, higher rotative speeds, higher engine temperatures, etc., have been concurrent with marked advances in methods of refining lubricant oils for automotive use. The demand for oils having lesser changes in viscosity with temperature change, that is, higher viscosity index, commonly referred to as V. I., has been met by refining lubricants intended for motor oils by certain solvent refining or solvent extraction processes. Certain liquid reagents possess solvent power for hydrocarbons of various types; as, for example, dichlorodiethyl ether, cresylic acid, phenol, chloraniline, chlorophenol, phenetidine, benzyl alcohol, nitrobenzene, benzonitrile, furfural, aniline, benzylacetate, liquid sulphur dioxide, mixtures of liquid sulphur dioxide or aniline with benzol, and the like. Those solvent refining processes are designed to concentrate in the desired lubricant fraction those compounds of a "paraffinic" nature possessed of

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the ability to suffer only a small change of viscosity, with changes of temperature, and to reject the compounds of "naphthenic" nature which do suffer such change of viscosity to a marked degree. These refining processes have provided a supply of an oil of quite desirable general characteristics definitely far superior to any oil previously produced from mixed base or asphaltic crudes, and superior to a like, though lesser, degree over oils previously produced from paraffin base crudes.

It has been found that the solvent refined motor oils referred to above are definitely corrosive to the newer bearing metals referred to above under normal conditions of automotive use, due to oxidation during use, sometimes resulting in bearing failure after only a few thousand miles of normal driving. It is further known that the same reaction, that is, corrosion of alloy-bearing metals such as cadmium-silver, also occurs in good paraffinic base oils which have not been subjected to solvent refining. The higher the V. I. of the lubricating oil, the more pronounced is the tendency to corrosion of the kind referred to above. Generally speaking, the problem is encountered in oils having a V. I. of 75 or higher, and becomes pronounced in oils having a V. I. of 80 to 85 or higher, and very pronounced in oils of 100 V. I. or higher.

Furthermore, the present trend in automotive design toward lower body styles, rapid acceleration, and the use of hypoid gears has increased the unit loadings on rear axles. In some cases the unit pressures encountered become great enough to rupture the oil film of ordinary mineral oil lubricants, with consequent metal to metal contact. In other lines of power transmission and the like, there is a similar tendency toward the use of high unit pressures of a degree which are near or beyond the limit at which mineral oils, alone, will maintain effective lubrication. The present invention is, therefore, specifically concerned with the production of lubricants capable of withstanding the high unit loadings which occur in such instances. Such lubricants are generally referred to as extreme pressure agents.

Lubricants of the extreme pressure type are normally produced by adding to a hydrocarbon lubricating oil a small amount of some characterizing substance which enables it to maintain a lubricant film unruptured under conditions which would cause the breakdown of a film formed of oil alone. Such additive substances are spoken of as E. P. (extreme pressure) bases, or E. P. ingredients. Many commonly used E. P. bases are composed of sulphur dissolved in min-

eral oil, sulphurized vegetable or animal oils, chlorinated compounds, metallic soaps, and the like. This invention is specifically concerned with the use, as E. P. characterizing ingredients, of reaction products new and novel for the purpose, and not hithertofore so used or known to be useful for this purpose.

It is an object of this invention to provide an extreme pressure lubricant, together with a base for use in compounding same, which lubricant is superior to lubricants of this class heretofore commonly known, particularly in load-carrying capacity, stability, and maintenance of extreme pressure lubricating properties under sustained conditions of high loading. It is an object of this invention to prepare novel and valuable ingredients and to combine them with hydrocarbon lubricant oils to produce lubricants having high load bearing capacities, to prepare such ingredients which have good characteristics of stability, and which are less corrosive than ordinary extreme pressure ingredients. Further objects are the provision of methods of preparing lubricants containing these novel characterizing ingredients and methods of lubrication making use of the lubricants so produced.

It is an important object of this invention to provide means for satisfactorily inhibiting or preventing corrosion from taking place to a serious degree particularly in oils of relatively high viscosity index. It is also an object of this invention to provide a substantially non-corrosive motor oil of high V. I. Still another object of the invention is to provide an additive reagent, or ingredient capable of inhibiting the corrosive properties of these oils. The production of solvent refined oils of low corrosive properties under conditions of automotive use is a major object of this invention, as well as the method of production of such oils which combine a relatively high viscosity index with a relatively low tendency to produce such corrosion.

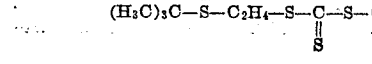
A further object is the provision of a method of lubrication making use of oils containing these novel ingredients.

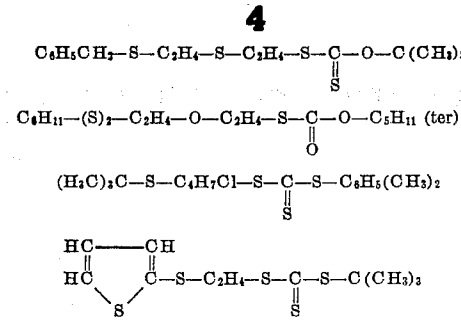
The present invention is predicated upon the discovery that hydrocarbon oils can be stabilized against the formation of acidic and/or corrosive bodies by oxidation in the presence of metal by the addition to said oils of a relatively small amount of a novel compound represented by the following general formula:

$$R'—A—R^2—B—R^3$$

wherein R′ and R^3 are monovalent hydrocarbon groups such as alkyl, alkenyl, cycloalkyl, cycloalkenyl, aralkyl, aralkenyl, alkaryl, alkenaryl, aryl, heteryl, etc., and at least one such group, either R′ or R^3 is a tertiary alkyl group; R^2 is a divalent hydrocarbon group of the aforesaid type (R′ and R^3) or a substituted group thereof such as a halogen-substituted alkyl group, an ether group, a thioether group, etc. A represents a thiocarbonate group, either mono-, di- or trithiocarbonate; and B represents either a thiocarbonate group, such as A, or a sulfide, either mono- or poly-sulfide. It will be understood from the foregoing that the terms "monovalent hydrocarbon group" (R′ and R^3) and "divalent hydrocarbon group" (R^2) are used generically and include all such groups as those recited above.

Typical of the compounds represented by the general formula are the following:





Compounds characterized by two tertiary alkyl groups, R′ and R^3 are outstanding when used in oil in small amounts, as demonstrated hereinafter by representative test data.

Inasmuch as these compounds are believed to be new and novel, they are also contemplated herein as new compositions of matter.

A typical and direct method of preparation of these compounds involves reaction of an organic dihalide and a mixture of a mercaptide and a thiocarbonate salt, as indicated in the following equation:

$$X—R_2—X+R_1—A—Na+R_3—S—Na\rightarrow R_1—A—R_2—S—R_3+2NaX$$

wherein X is a halogen atom.

This method is illustrated by the following examples:

EXAMPLE I

(a) Preparation of a sodium tertiary butyl thiocarbonate-sodium tertiary mercaptide equimolar mixture

A solution of 600 grams of tertiary butyl mercaptan in 3,000 cc. of benzol was treated by adding dropwise thereto 281 grams of 95% sodium hydroxide in 400 cc. of water, in a 5-liter 3-necked flask fitted with a water take-off condenser, an electric stirrer and a dropping funnel. The stirred reaction mixture was refluxed at 80–85° C. with water removal for 13½ hours by heating the flask with a hot water bath. The water take-off was replaced by a condenser after cooling the flask to about 10° C. and thereafter 900 grams of carbon disulfide were slowly introduced to the stirred suspension. The reaction mixture was then refluxed at 50–60° C. for two hours and then allowed to cool. The reaction mixture was filtered, and the filtrate therefrom was washed with petroleum ether whereupon a light yellow powdery material was obtained. This material contains 41.4% sulphur as compared with the calculated value of 42.7% for a equimolar mixture of the mercaptide and trithiocarbonate.

(*b*) A solution of 510 grams of equimolar mixture prepared in (*a*) above, in 1,600 ccs. of isopropyl alcohol was refluxed at 82–87° C. with 173 grams of β,β′ dichloro-diethyl ether for a period of 8 hours whereupon a salt was formed. The salt formed was removed by filtration and washed with hot isopropyl alcohol. The alcohol solution from the washing procedure and from the reaction filtrate was diluted with an equal volume of water to cause a direct separation of a reddish oil as a lower layer. The upper and aqueous layer was extracted also with petroleum ether and these extracts were added to the original recovered red oil. The combined red oil solution was then distilled to a maximum liquid temperature of 160° C. at 20–30 mm. to remove petroleum ether and other volatile impurities. The final product was a red oil weighing 245 grams, corresponding to a 48.9 per cent yield based on chlorex used. The oil

contains 36.4 per cent sulphur as compared with the calculated value of 39.4 per cent for $(H_3C)_3CSCS_2CH_2CH_2OCH_2CH_2SC(CH_3)_3$.

EXAMPLE II

An equimolar mixture, 1175 grams, of sodium tertiary butyl mercaptide and sodium tertiary butyl trithiocarbonate prepared as indicated in Example I(*a*) above, was charged into a 22-liter flask with 8 liters of isopropyl alcohol and 375 grams of ethylene dichloride. The reaction mixture was heated by a hot water bath and vigorously stirred by an electrically driven stirrer. The reaction mixture was warmed slowly to the reflux temperature, 82–87° C., and was refluxed for 30 hours. The reaction mixture was filtered while warm in order to remove salt which separated therefrom, and the filtrate was separated into two layers, a lower brine layer and an upper isopropyl alcohol layer containing the reaction product. The isopropyl alcohol solution or layer was heated and stirred to remove most of the isopropyl alcohol. The concentrated product was water-washed and thereafter distilled to a maximum temperature of 130° C. at 20 mms., with nitrogen gas being used to sweep out the vapors. The residue, the non-volatile portion, was chilled to −5° C. whereupon yellow crystals separated therefrom. These crystals were removed by filtration thereby providing a filtrate and the yellow crystals. The filtrate contains 44.9 per cent sulphur as against 45.6 per cent sulphur calculated for $(H_3C)_3CSCS_2CH_2CH_2SC(CH_3)_3$. The yellow solid was recrystallized from Stoddard solvent, washed with petroleum ether and distilled under vacuum to remove said solvent and ether. The purified yellow solid contained 54.3 per cent sulfur and had a molecular weight of 368–371, as compared with 53.8 per cent sulfur and molecular weight 358, respectively, for $(H_3C)_3CSCS_2CH_2CH_2S_2CSC(CH_3)_3$.

To demonstrate the effectiveness of compounds of the type contemplated herein, unblended oils and blends thereof containing small amounts of such compounds were subjected to the following corrosion tests: an oil was tested by adding a section of a bearing containing a cadmium-silver alloy surface and weighing about 6 grams and heating it to 175° C. for 22 hours while a stream of air was bubbled against the surfaces of the bearing. The loss in weight of the bearing during this treatment measures the amount of corrosion that has taken place. A sample of the oil containing a characterizing compound was run at the same time as a sample of the straight oil and the loss in weight of the bearing section in the inhibited oil could thus be compared directly with the loss of the section in the uninhibited oil. The oil used consisted of a Pennsylvania neutral and residual stock separately refined by means of chlorex and then blended to give an SAE 20 motor oil with a specific gravity of 0.872, a flash point of 435° F., and a Saybolt Universal viscosity of 318 seconds at 100° F. The results obtained in this test are set forth in Table I below:

Table I

Compound	Conc., Wt. per cent	Mgs. Loss in Wt.	
		Inhibited	Uninhibited
(*n*) $H_9C_4-S-\underset{\underset{S}{\|}}{C}-S-C_2H_4-S-C_4H_9$ (*n*)	0.5	35	33
$(H_3C)_3C-S-\underset{\underset{S}{\|}}{C}-S-C_2H_4-S-C(CH_3)_3$	0.5	2	40
	1.0	0	40
$(H_3C)_3C-S-\underset{\underset{S}{\|}}{C}-S-C_4H_7Cl-S-C(CH_3)_3$	0.25	0	30
	0.5	0	30
$(H_3C)_3C-S-\underset{\underset{S}{\|}}{C}-S-C_5H_{10}-S-C(CH_3)_3$	0.5	0	30
(ter) $H_{11}C_5-S-\underset{\underset{S}{\|}}{C}-S-C_2H_4-S-C_5H_{11}$ (ter)	0.5	3	33
$(H_3C)_3C-S-\underset{\underset{S}{\|}}{C}-S-C_2H_4-S-\underset{\underset{S}{\|}}{C}-S-C(CH_3)_3$	0.1	7	33
	0.25	0	33
	0.5	0	33

As hereinabove mentioned, the novel compounds contemplated herein are effective extreme pressure (E. P.) agents. Oil blends containing typical characterizing compounds were subjected to the Almen pin test (described by Wolf and Mougey, Proc. A. P. I. 1932, pp. 118–130) and the SAE test (described Anon S. A. E. Journal 39, 23–4, 1936) with the results as shown in Table II below, wherein the oil used was a mineral oil of 80–90 seconds S. U. V. at 210° F.

Table II

Compound	Conc., Wt. per cent	Almen pin test load limit, lbs.	S. A. E. Test load limit, lbs. (1000 R. P. M.)
None	----------	3,000–4,000	10–15
$(H_3C)_3C-S-\underset{\underset{S}{\|}}{C}-S-C_2H_4-S-C(CH_3)_3$	10	26,000	560
$(H_3C)_3C-S-\underset{\underset{S}{\|}}{C}-S-C_4H_8Cl-S-C(CH_3)_3$	10	21,000	560

The proportion of the characterizing compounds of this invention used in admixture with ordinary hydrocarbon oils may be varied considerably. Generally, concentrations of from about 0.05 per cent to about 5 per cent of the compounds effectively stabilize the oils in which they are used. Ordinary hydrocarbon oils are effectively fortified to withstand extreme pressure conditions now encountered in hypoid gears and the like, when concentrations from about 5 per cent to about 15 per cent are used. In general, then, these compounds are used in amounts ranging from about 0.05 per cent to about 15 per cent depending upon the oil used and the improvement desired. Further, these characterizing compounds may also be used in oil in combination with other oil-addition agents such, for example, as pour point depressants, viscosity index improving agents, other antioxidants such, for example, as phenols, amines, etc.

This application is a division of application Serial Number 613,704, filed August 30, 1945.

It will be understood that the present invention is not restricted to the details of the foregoing examples which are presented herein to illustrate the invention, rather the invention is to be construed broadly in the light of the defining language of the appended claims.

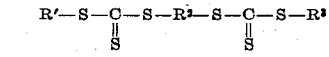
We claim:

1. As a new composition of matter, a compound represented by the general formula:

$$R'—A—R^2—B—R^3$$

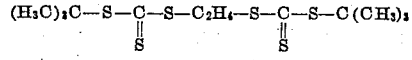
wherein R′ and R^3 are monovalent tertiary alkyl groups; R^2 is an alkylene group; and wherein A is a trithiocarbonate group and B is selected from the group consisting of a sulfide group and a trithiocarbonate group.

2. As a new composition of matter, a compound represented by the general formula:

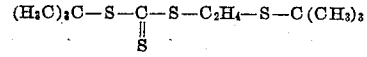


wherein R′ and R^3 represent monovalent tertiary alkyl groups and R^2 represents an alkylene group.

3. As a new composition of matter, the compound:



4. As a new composition of matter:



DARWIN E. BADERTSCHER.
CHARLES F. FEASLEY.
HENRY G. BERGER.

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