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STABILIZED HYDROCARBON PRODUCTS

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19 Claims. (Cl. 252—32.7)

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This invention relates to a new class of chemical compositions having marked anti-oxidant properties when incorporated in hydrocarbon products, and it relates more particularly to the use of such compositions in mineral lubricating oils.

In my co-pending application Serial No. 635,112, filed December 14, 1945, now U. S. 2,436,589, I disclosed my discovery that zinc isopropyl xanthate possesses the property of inhibiting the oxidation and consequent development of corrosive properties in mineral lubricating oils to a very remarkable degree, and that the compound also promotes general engine cleanliness when oils containing it are used as crankcase lubricants for internal combustion engines. This agent is free from the corroding tendencies which have been observed when metal derivatives of fatty acids, sulfonic acids, phenols and the like have been used.

One difficulty encountered in the commercial use of zinc isopropyl xanthate as an additive for lubricating oils is the fact it is difficult to dissolve more than about 0.5% by weight of this compound in oil. For many purposes, it would be desirable to employ concentrations greater than 0.5%, and even where this amount or less is required in the oil blend, a compound of increased solubility could be dissolved in an oil in much shorter time and with greater ease. It is accordingly an object of the present invention to provide a composition which is a chemical combination of zinc isopropyl xanthate or a similar metal xanthate compound with another compound which markedly increases the solubility in oil and at the same time provides the requisite anti-oxidant properties. It has been found that zinc isopropyl xanthate and the like may thus be combined with organo-substituted thiophosphorous and thiophosphoric acids and their organic nitrogen base salts. Such thiophosphorous and thiophosphoric acids and their salts when used alone as mineral oil additives exhibit a tendency to stain copper and to separate from the oil on contact with small quantities of water.

It has been found, in accordance with the present invention, that by heating a mixture of zinc isopropyl xanthate with an organo-substituted thiophosphorous or thiophosphoric acid or an organic nitrogen base salt of the same, e. g.,

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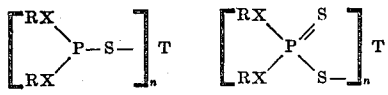
the isopropylamine salt of tert.-octylphenyl thiophosphoric acid, at a slightly elevated temperature, of the order of about 110° C., the two compounds will fuse together to form a homogeneous mass, and the product will remain homogeneous on cooling. It is therefore believed that a chemical combination of the two compounds has taken place, and the reaction appears to be one of simple addition, since there is no evidence of the formation of any by-products. The reaction may also be brought about by heating the reactants together in an inert organic medium such as a mineral oil. In preparing compounds of this type it is only necessary to heat the two salts together until a homogeneous solution is obtained, which requires 10 to 15 minutes, and then to filter to remove a slight amount of insoluble material, or to heat the reactants together in the presence of a solvent for the product, such as a mineral lubricating oil, until complete solution has taken place.

The "adducts" or double salts prepared as described above have been found to be very soluble in mineral oil. In fact, by combining zinc isopropyl xanthate with the thiophosphorous or thiophosphoric acids or salts herein described, it has been found that 10% or more of the zinc isopropyl xanthate may be dissolved in the oil. It has also been found that the combination salts exhibit good general antioxidant properties and do not have the copper-staining and water sensitive characteristics of the thiophosphorous and thiophosphoric acids or salts thereof which are observed when these compounds are used alone. The double salts, in other words, are excellent agents for inhibiting oxidation generally in a wide variety of non-aromatic type hydrocarbon products, as will be disclosed more fully hereinafter.

The metal xanthate compounds which may be employed in accordance with this invention are the metal alkyl xanthates containing metals of Groups I and II of the Periodic Table and having alkyl groups of at least two carbon atoms. These alkyl groups may be straight or branched. Such compounds may be prepared by treating an alcohol, e. g., isopropyl alcohol, with potassium or sodium hydroxide and carbon disulfide. If a salt of a Group II metal is desired, the alkali metal xanthate may be reacted with a soluble

salt of the metal in question. Examples of such metal xanthate compounds are zinc isopropyl xanthate, zinc ethyl xanthate, zinc iso-octyl thioxanthate, potassium butyl xanthate, potassium amyl xanthate, barium cetyl thioxanthate, and cadmium lauryl xanthate.

The organo-substituted thiophosphorous and thiophosphoric acids and salts which may be combined with the metal alkyl xanthate in accordance with this invention may be represented by the formulas



in which R represents an oil-solubilizing organic group containing at least one alkyl group of at least three carbon atoms, X represents a non-metallic element of Group VI of the Periodic Table, T is a member of the class consisting of hydrogen and organic nitrogen base radicals, and n is a number equal to the valence of T. The more preferred compounds are the thiophosphorous and thiophosphoric acids or salts thereof containing alkyl groups of about 5 to 18 carbon atoms connected through oxygen atoms to phosphorus. In the above formulas R may represent a straight or branched chain alkyl group or an alkyl group substituted with sulfur, oxygen, halogens or the like, or aryl groups containing alkyl side chains, and such groups may also contain substituent atoms or groups. Examples of particularly suitable compounds of this type are isopropyl thiophosphoric acid, tert.-octylphenyl thiophosphoric acid, tert.-octylphenyl thiophosphorous acid, isopropylamine salt of tert.-octylphenyl thiophosphorous acid, and the like.

The thiophosphorous and thiophosphoric acids of the present invention may be prepared by reacting the corresponding alcohols or phenols with phosphorus heptasulfide (P_4S_7) or phosphorus pentasulfide (P_2S_5), respectively. The reaction is brought about merely by heating the reactants together or preferably in the presence of a solvent such as a light mineral oil. Suitable alcohols and phenols include saturated straight chain or branched chain alcohols, sulfurized alcohols, chlorinated alcohols, commercial mixtures of higher alcohols, (e. g., a mixture of higher alcohols having from 12–16 carbon atoms per molecule), alcohols obtained in the oxidation of petroleum hydrocarbons, cyclic alcohols, and the like. Suitable phenols are the alkylated phenols containing one or more alkyl groups. Such phenols include such compounds as tert.-amyl phenol, isohexyl phenol, tert.-octylphenol, di-tert.-amyl phenol, and the like. Simple phenols will not exhibit the requisite oil solubility.

In preparing organic nitrogen base salts of the thiophosphorous and thiophosphoric acids described above, any organic nitrogen base may be employed, but the most preferred bases are the primary and secondary aliphatic amines. Other amines such as tertiary aliphatic amines, quaternary ammonium hydroxides or aromatic amines may also be used. The acids are neutralized merely by bringing the amines into contact therewith, preferably by gradual addition in the presence of a suitable solvent. Specific examples of suitable amines include methylamine, isopropylamine, diethylamine, aniline, ethylaniline, benzylamine, ethyl naphthylamine,

p-phenylenediamine, and the heterocyclic amines such as pyridine and piperidine.

In preparing the combination salts described above it is generally most advantageous to employ from about 10% to 25% of the xanthate compound in the total salt mixture. The amount of the final product which is most advantageously employed in lubricating oils and other products will vary according to the purpose in adding the composition and the nature of the basic material; but generally when the composition is to be employed as a corrosion inhibitor and detergent in crankcase lubricating oils, the amount is from about 0.02% to about 2%, preferably from 0.1% to 1.0%. For convenient shipping and storage of the additives prior to incorporation in the lubricating oil base, it is desirable to prepare concentrates containing 25 to 50% of the double salts. When these double salts are prepared by reacting the component salts in an oil medium, the reaction product consisting of an oil solution may conveniently be employed as a commercial concentrate.

In the following examples are described methods of preparing individual compounds of the type described above as well as the combination salts, and tests of the effect of the individual compounds and combination salts as corrosion inhibitors in lubricating oils. These examples are not to be considered as limiting the scope of the invention in any way.

Example 1.—Preparation of isopropyl thiophosphoric acid

A mixture of 6.0 g. of isopropanol, 5.5 g. of P_2S_5, and 41.1 g. of a refined light lubricating oil of approximately SAE—10 grade was heated in a 3-necked 500 cc. flask equipped with a stirrer, reflux condenser, and thermometer, at 140° C., until the P_2S_5 had reacted (about 1 hour). The product was then filtered to remove a small amount of insoluble material. The clear, dark brown filtrate possessed a strong H_2S odor.

Example 2.—Preparation of C_{12}–C_{16} alkyl thiophosphoric acid

A mixture of 10.7 g. of a commercial mixture of C_{12} to C_{16} alcohols, 2.8 g. of P_2S_5, and 33.5 g. of a refined light lubricating oil of approximately SAE—10 grade was heated in a 125 cc. beaker with stirring at 140° C. until the P_2S_5 had reacted (about 40 minutes), after which the product was filtered to remove a small amount of insoluble material. The clear, dark brown filtrate possessed a strong H_2S odor.

Example 3.—Preparation of tert.-octylphenyl thiophosphoric acid

The tert.-octylphenyl thiophosphoric acid was prepared in the manner described in Example 2, using 10.3 g. of tert.-octyl phenol, 2.8 g. of P_2S_5, and 31.5 g. of a refined light lubricating oil of approximately SAE—10 grade. The clear dark brown product possessed a strong H_2S odor.

Example 4.—Preparation of tert.-octylphenyl thiophosphorous acid

The tert.-octylphenyl thiophosphorous acid was prepared in the manner described in Example 2, using 10.3 g. of tert.-octyl phenol, 2.1 g. of P_4S_7, and 30.6 g. of a refined light lubricating oil of approximately SAE—10 grade. The clear, dark yellow product possessed a very strong odor of H_2S.

Example 5.—Preparation of zinc isopropyl xanthate-thiophosphoric acid and-thiophosphorous acid double salts

The double salts were prepared by heating the oil solutions of the thiophosphoric acid and thiophosphorous acid, respectively, (prepared as described in Examples 1–4) with zinc isopropyl xanthate (mol per mol ratio) at 110° C., until solution was obtained (about 10 minutes), followed by filtration to remove a small amount of insoluble material.

The products were light yellow or light brown, possessing practically no odor.

Example 6.—Preparation of isopropylamine tert.-octylphenyl thiophosphate

A mixture of 847 g. of a refined light lubricating oil of approximately SAE—10 grade and 412 g. of tert.-octyl phenol was placed in a 3-necked 3-litre flask equipped with a stirrer, reflux condenser, and thermometer. The mixture was heated with stirring until a homogeneous solution was obtained (temperature about 80° C.). 111 g. of P_2S_5 was was then added and the temperature was raised to 140° C. at which point it was held for 4 hours. The reaction product was then filtered to remove a small amount of insoluble material. Upon cooling to room temperature, the filtrate was poured into a 3-necked 3-litre flask equipped with a stirrer, reflux condenser, and dropping funnel. 59 g. of isopropylamine was then added dropwise over a period of 1 hour, after which the reaction product was stirred for an additional hour. The product was then filtered and placed on the steam bath with nitrogen blowing for 18 hours. The clear, pale red concentrate showed the following analysis:

	Found	Calculated
	Per cent	*Per cent*
Phosphorus	2.01	2.19
Sulfur	3.91	4.42

Example 7.—Preparation of zinc isopropyl xanthate-isopropylamine tert.-octylphenyl thiophosphate double salt

A mixture of isopropylamine tert.-octylphenyl thiophosphate concentrate (containing 1 mol of salt) and zinc isopropyl xanthate (0.5 mol) was heated at 110° C. until solution was obtained (about 10 minutes), followed by filtration to remove a small amount of insoluble material. A clear, practically odorless product was obtained.

Example 8.—Preparation of isopropylamine tert.-octylphenyl thiophosphite

The tert.-octylphenyl thiophosphorous acid was prepared according to the procedure described in Example 6, using 412 g. of tert.-octyl phenol, 661 g. of a refined light lubricating oil of approximately SAE—10 grade, and 87 g. of P_4S_7. A solution of 59 g. of isopropylamine in 150 g. of the lubricating oil solvent was then added to the oil solution of tert.-octylphenyl thiophosphorous acid over a period of 1½ hours, after which the preparation was completed in the manner described in Example 6. The light yellow concentrate showed the following analysis:

	Found	Calculated
	Per cent	*Per cent*
Phosphorus	2.55	2.29
Sulfur	3.29	3.10

Example 9.—Preparation of zinc isopropyl xanthate-isopropylamine tert.-octylphenyl thiophosphite double salt

A mixture of isopropylamine tert.-octylphenyl thiophosphite concentrate (containing 1 mol) and zinc isopropyl xanthate (1 mol) was heated at 110° C. until solution was obtained (about 10 minutes) followed by filtration to remove a small amount of insoluble material. The isopropylamine tert.-octylphenyl thiophosphite alone tends to decompose during prolonged storage, evolving H_2S. The clear, practically odorless double salt with zinc isopropyl xanthate is stable, showing no evidence of decomposition or H_2S evolution during extended storage.

Example 10.—Preparation of isopropylamine-C_{12}–C_{16} alkyl thiophosphate

The alkyl thiophosphoric acid was prepared according to the procedure described in Example 6 using 428 g. of a commercial mixture of C_{12} to C_{16} alcohols, 721 g. of a light refined lubricating oil of approximately SAE—10 grade and 111 g. of P_2S_5. A solution of 59 g. of isopropylamine in 150 g. of the lubricating oil solvent was then added to the oil solution of the alkyl thiophosphoric acid over a period of 1½ hours, after which the preparation was completed in the manner described in Example 6. The clear, pale brown concentrate showed the following analysis:

	Found	Calculated
	Per cent	*Per cent*
Phosphorus	1.87	2.13
Sulfur	3.65	4.2

Example 11.—Preparation of zinc isopropyl xanthate-isopropylamine C_{12}–C_{16} alkyl thiophosphate double salt

A mixture of isopropylamine alkyl thiophosphate concentrate prepared as in Example 10 (containing 1 mol of salt) and zinc isopropyl xanthate (1 mol) was heated at 110° C. until solution was obtained (about 10 minutes) followed by filtration to remove a small amount of insoluble material. The isopropylamine alkyl thiophosphate undergoes a slow decomposition during prolonged storage, liberating H_2S. The double salt formed with zinc isopropyl xanthate is practically odorless and very stable, evolving no H_2S upon extended storage.

Example 12.—Laboratory bearing corrosion tests

Blends of various individual organo-substituted thiophosphorous and thiophosphoric acids and amine salts as well as of the double salts prepared by reacting such compounds with zinc isopropyl xanthate, as in the foregoing examples, in a lubricating oil base were submitted to a corrosion test designed to measure the effectiveness of the products in inhibiting the corrosiveness of a typical mineral lubricating oil toward the surfaces of copper lead bearings. The base oil employed was a refined solvent extracted paraffinic type mineral lubricating oil of SAE—20 viscosity grade and each blend contained 0.25% by weight of additive. The test was applied also to the unblended base oil. 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 facili-

tate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° C. 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 4-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 4-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. The unblended base oil showed a corrosion life of 8 hours.

Additives	Bearing Corrosion Life, Hrs.	
	Alone	Combined with Zinc Isopropyl Xanthate
Isopropyl thiophosphoric acid	-------	34
C_{12}-C_{18} alkylthiophosphoric acid (Exs. 2 and 5)	-------	25
tert.-Octylphenyl thiosphorous acid	-------	27
tert.-Octylphenyl thiophosphoric acid	-------	22
Isopropylamine tert.-octylphenyl thiophosphite	34	29
Isopropylamine tert.-octylphenyl thiophosphate	22	56
Isopropylamine C_{12}-C_{16} alkyl thiophosphate (Exs. 10 and 11)	14	22

In the above series of tests no tests were made of the various thiophosphorous and thiophosphoric acids which were not combined with zinc isopropyl xanthate, since the uncombined acids are quite unsuitable as lubricating oil additives, being very corrosive to copper and having a very objectionable odor. The results of the tests show in general a superiority in the combination or double salts.

Example 13.—Lauson engine tests

An example of double salt additives of the present invention in this case the combination of zinc isopropyl xanthate with isopropylamine tert.-octylphenyl thiophosphate, was tested as to its effectiveness in reducing varnish formation and in inhibiting bearing corrosion in a Lauson engine by comparing the effects produced by a base oil consisting of a solvent extracted Mid-Continent paraffinic oil containing a viscosity index improver and having a viscosity index of 125 and a viscosity at 210° F. of 52 seconds with the effects of the same oil containing 0.64% of the additive described in a 20 hour test in the Lauson engine, operated at 300° F. jacket temperature, 295° F. oil temperature, 1800 R. P. M. speed and 1.5 indicated kilowatt load. The amount of varnish deposited on the piston surfaces is shown by a demerit system of rating wherein a perfectly clean surface is given a rating of 0 and a demerit of 10 is given to the worst condition which could be expected to exist on such surfaces. The bearing weight loss in the copper-lead bearing is indicated by showing the direct loss of weight in milligrams. The results of these tests are as follows:

Oil Tested	Varnish Demerit	Cu-Pb Bearing Weight Loss (mg./bearing)
Base Oil	4.25	80
Base Oil+0.64% zinc isopropyl xanthate—isopropylamine tert.-octylphenyl thiophosphate double salt	3.20	20

The products of the present invention may be employed not only as the sole additives in hydrocarbon lubricating oils but also in conjunction with such detergent type additives as metal sulfonates, metal soaps, metal phenates, metal alcoholates, metal phenol sulfonates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, reaction products of metal phenates or metal phenol sulfides with sulfur, reaction products of metal phenates or metal phenol sulfides with phosphorus sulfides and the like. Thus, the new additives of this invention may be used in lubricating oils containing such addition agents as nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amyl phenol sulfide, calcium petroleum sulfonate, zinc methyl cyclohexyl thiophosphate, calcium dichlorostearate, etc.

The lubricating oil base stocks 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, for example, by solvent extraction with solvents of the type of phenol, surfur dioxide, furfural, dichlorethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic 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. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives 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 or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular

use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engine service, oils of higher viscosity index are often required, for example up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, defoaming or anti-foaming agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable as plasticizers and defoaming agents are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight or branched chain aliphatic alcohols such as octyl alcohols ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol, ($C_{18}H_{37}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol; or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also used mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

The double salts of the present invention are useful as antioxidants in various other hydrocarbon materials, such as extreme pressure lubricants, greases, hydraulic fluids, motor fuels, kerosene, paraffin waxes, hydrocarbon polymers, natural and synthetic rubbers, and the like.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

I claim:

1. A mineral oil containing an oxidation inhibiting amount of a double salt prepared by fusing together a metal alkyl xanthate, in which the metal is selected from Groups I and II of the Periodic Table and in which the alkyl group

contains at least two carbon atoms, and a compound selected from the group consisting of organo thiophosphorous and thiophosphoric acids and their organic nitrogen base salts having the formulas—



respectively, in each of which formulas R represents an organic group selected from the class consisting of alkyl radicals and alkaryl radicals and containing at least one alkyl radical of at least three carbon atoms, X represents a non-metallic element of Group VI of the Periodic Table, T represents a member of the group consisting of hydrogen and organic nitrogen base radicals, and n is a number equal to the valence of T, in the ratio of one-half to one molecular proportion of the xanthate compound to one molecular proportion of the phosphorus-containing compound.

2. A composition according to claim 1 in which the mineral oil is a mineral lubricating oil.

3. A composition according to claim 1 in which the mineral oil is a mineral lubricating oil and in which the metal alkyl xanthate is zinc isopropyl xanthate.

4. A mineral lubricating oil containing an oxidation inhibiting amount of a double salt prepared by fusing together a metal alkyl xanthate in which the metal is selected from Group II of the Periodic Table and in which the alkyl group contains at least two carbon atoms, and an organo substituted thiophosphoric acid wherein each organic group is selected from the class consisting of alkyl and alkaryl radicals, each containing at least one alkyl group of at least three carbon atoms, in the ratio of one-half to one molecular proportion of the xanthate compound to one molecular proportion of the thiophosphoric acid.

5. A mineral lubricating oil containing an oxidizing inhibiting amount of a double salt prepared by fusing together a metal alkyl xanthate in which the metal is selected from Group II of the Periodic Table and in which the alkyl group contains at least two carbon atoms, and an organic nitrogen base salt of an organo-substituted thiophosphoric acid in which each organic group is selected from the class consisting of alkyl radicals and alkaryl radicals, each containing at least one alkyl group of at least three carbon atoms, in the ratio of one-half to one molecular proportion of the xanthate compound to one molecular proportion of the thiophosphate.

6. A mineral lubricating oil according to claim 4 in which the metal alkyl xanthate is zinc isopropyl xanthate.

7. A mineral lubricating oil according to claim 5 in which the metal alkyl xanthate is zinc isopropyl xanthate.

8. A mineral lubricating oil containing an oxidation inhibiting proportion of a double salt prepared by fusing together one-half to one molecular proportion of zinc isopropyl xanthate and one molecular proportion of an alkyl thiophosphoric acid in which the alkyl groups each contain 12–16 carbon atoms.

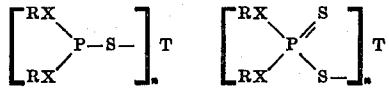
9. A mineral lubricating oil containing an oxidation inhibiting proportion of a double salt prepared by fusing together one-half molecular proportion of zinc isopropyl xanthate and one molecular proportion of tert.-octylphenyl thiophosphoric acid.

10. A mineral lubricating oil containing an oxidation inhibiting proportion of a double salt prepared by fusing together equal molecular proportions of zinc isopropyl xanthate and isopropyl thiophosphoric acid.

11. A mineral lubricating oil containing an oxidation inhibiting proportion of a double salt prepared by fusing together equal molecular proportions of zinc isopropyl xanthate and the isopropylamine salt of tert.-octylphenyl thiophosphoric acid.

12. A concentrated mineral oil solution containing 25 to 50% by weight of a double salt defined as in claim 2.

13. As a new composition of matter a double salt prepared by fusing together one-half to one molecular proportion thereof a metal alkyl xanthate, in which the metal is selected from Groups I and II of the Periodic Table and in which the alkyl group contains at least two carbon atoms, and one molecular proportion of a compound selected from the group consisting of organo thiophosphorous and thiophosphoric acids and their organic nitrogen base salts having the formulas



respectively, in each of which formulas R represents an organic group selected from the class consisting of alkyl radicals and alkaryl radicals, each containing at least one alkyl radical of at least three carbon atoms, X represents a nonmetallic element of Group VI of the Periodic Table, T represents a member of the group consisting of hydrogen and organic base radicals, and n is a number equal to the valence of T.

14. As a new composition of matter a double salt according to claim 13 in which the metal alkyl xanthate is zinc isopropyl xanthate.

15. As a new composition of matter a double salt prepared by reacting together one-half to one molecular proportion of a metal alkyl xanthate in which the metal is selected from Group II of the Periodic Table and in which the alkyl group contains at least two carbon atoms and one molecular proportion of an organo-substituted thiophosphoric acid in which the organic groups are selected from the class consisting of alkyl radicals and alkaryl radicals, each containing an least one alkyl group of at least three carbon atoms.

16. As a new composition of matter a double salt prepared by reacting together one-half to one molecular proportion of a metal alkyl xanthate in which the metal is selected from Group II of the Periodic Table and in which the alkyl group contains at least two carbon atoms, and one molecular proportion of an organic amine salt of an organo-substituted thiophosphoric acid in which the organic groups are selected from the class consisting of alkyl radicals and alkaryl radicals, each containing at least one alkyl group of at least three carbon atoms.

17. As a new composition of matter a double salt prepared by fusing together equal molecular proportions of zinc isopropyl xanthate and isopropyl thiophosphoric acid.

18. As a new composition of matter a double salt prepared by fusing together equal molecular proportions of zinc isopropyl xanthate and tert.-octylphenyl thiophosphoric acid.

19. As a new composition of matter a double salt prepared by fusing together one-half molecular proportion of zinc isopropyl xanthate and one molecular proportion of the isopropyl amine salt of tert.-octylphenyl thiophosphoric acid.

JOHN P. McDERMOTT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,034,665	Ott	Mar. 17, 1936
2,133,828	Moran	Oct. 18, 1938
2,199,944	Peski et al.	May 7, 1940
2,226,420	Badertscher et al.	Dec. 24, 1940
2,252,985	Rutherford et al.	Aug. 19, 1941
2,311,306	Ritchey	Feb. 16, 1943
2,315,072	Nelson et al.	Mar. 30, 1943
2,354,536	Nelson	July 25, 1944
2,368,670	Lincoln et al.	Feb. 6, 1945
2,380,400	Browning	July 31, 1945