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COMPOUNDED OIL

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This invention relates to a new and useful composition of matter. More particularly, the invention relates to viscous hydrocarbon oils containing a new combination of stabilizing agents which give a synergetic effect. This combination comprises an anti-oxidant and an activator therefor which increases the effectiveness of the anti-oxidant even though the activator alone may have substantially no anti-oxidant action in the oil being stabilized.

The production of improved hydrocarbon oils, and particularly of lubricating oils having desired characteristics, has been the subject of extensive research and investigation. A characteristic which has been found particularly significant is the tendency of hydrocarbon oils to deteriorate or partially oxidize when subjected to high temperatures. It is important that resistance to such deterioration or oxidation be imparted to hydrocarbon oils, particularly to lubricating oils, in order that such compositions may be relatively free from the tendency to form sludge and other types of deposits.

A direct result of oxidation and deterioration of oils during lubrication of internal combustion engines is the tendency of the oil to cause or permit the sticking of piston rings or the deposition of adhesive varnish-like material on the cylinder walls of the engine. The crankcase lubricant in internal combustion engines is subjected to extremely severe operating conditions, and in engines of the Diesel type the lubricant encounters in the piston ring zone temperatures of from approximately 425° F. to approximately 650° F. and pressures from oxidizing combustion gases as high as 750 to 1150 pounds per square inch. In its more specific aspects, the present invention is directed to the improvement of hydrocarbon oils by imparting thereto increased resistance to oxidation at temperatures in the order of those above mentioned. Anti-oxidants which are effective at lower temperatures often become ineffective at higher temperatures, such as 300° F. or above. Even those anti-oxidants which are effective to stabilize hydrocarbon oils against oxidation at 300° F. are often unable to impart to the oil sufficient stability to withstand these severe conditions for more than a relatively short period of time.

The development of the lubricating art has resulted in the use of highly refined and highly paraffinic type lubricating oils. This development seems not to have helped in the solution of the problem of stabilizing the lubricants against oxidation since the highly refined or highly paraffinic lubricating oils are more difficult to satisfactorily stabilize, without introducing other undesirable properties, than were the less highly refined naphthenic base lubricating oils.

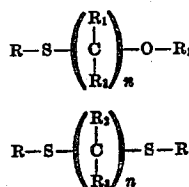
This invention provides a combination of com-

pounding agents capable of imparting to such highly paraffinic and/or other highly refined oils a high stability against oxidation or deterioration, even at 300° F. or above. Further, the invention provides a combination of compounding agents which does not increase the corrosivity of naturally non-corrosive lubricating oils and which actually reduces or inhibits the corrosive action that develops with certain highly paraffinic or highly refined lubricating oils.

The combination of the invention comprises an anti-oxidant of the type represented by di-alkyl thioethers and an activating agent for the anti-oxidant. Examples of thioethers operative for the purpose of the invention are high molecular weight di-alkyl thioethers containing at least one long carbon chain. By "long carbon chain" is meant a radical containing at least 8 to 10 carbon atoms. By "high molecular weight thioethers" it is intended to designate thioethers containing in the order of a total of 12 or more carbon atoms. Examples of such high molecular weight di-alkyl thioethers are the following monothioethers: di-octyl thioether; octyl decyl thioether; octyl dodecyl thioether; octyl tetra-decyl thioether; octyl cetyl thioether; di-decyl thioether; decyl dodecyl thioether; decyl tetra-decyl thioether; decyl cetyl thioether; di-dodecyl thioether; dodecyl tetra-decyl thioether; dodecyl cetyl thioether; di-tetra-decyl thioether; tetra-decyl cetyl thioether; di-cetyl thioether; di-octadecyl thioether. The preferred di-alkyl monothioethers contain one long chain and one short chain, for example, dodecyl methyl monothioether, dodecyl ethyl monothioether, dodecyl propyl monothioether; tetra-decyl methyl monothioether, tetra-decyl ethyl monothioether, tetra-decyl propyl monothioether; cetyl methyl monothioether, cetyl ethyl monothioether, cetyl propyl monothioether.

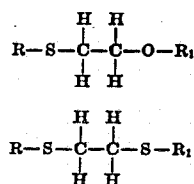
The above compounds are represented by the type formula $R-S-R_1$, where R and R_1 may be the same or different alkyl radicals. R and R_1 may be either a straight hydrocarbon chain or a branched chain such as obtained from isobutylene polymers or interpolymers of butylene with isobutylene and other analogous olefin polymer derivatives.

Monothio or dithio di-alkyl di-ethers of the general formulae:

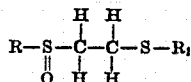


for example, monothioethane di-alkyl di-ethers,

or dithioethane di-alkyl di-ethers, are also effective in the combination of this invention. These latter compounds may be represented by the formulae:

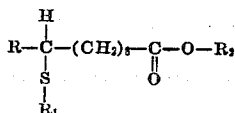


where R and R₁ may be any of the alkyl radicals previously listed above for these radicals, R₂ and R₃ may be either hydrogen or any one of such alkyl radicals and n may be any whole number. Sulfoxides such as—



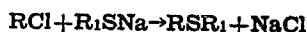
are not precluded.

It is to be understood that the invention in its broader aspects does not preclude the use of substituted alkyl radicals in the thioether component of the composition. However, when such a substituent is present it should not be so close to the sulfur atom of the thioether group as to substantially destroy the essential thioether characteristics of the sulfur atom. Thus, functional groups in the alkyl radicals of thioether which are positioned on the alkyl chain relatively remote from the thioether sulfur atom may be utilized. For example, thioethers derived from oleic acid esters are effective compounds in the combination of this invention. This type of compound may be represented by the formula:



where R, R₁ and R₂ are alkyl radicals, R₁ preferably being a relatively short chain such as an ethyl group. The carbonyl group of the above type compound is sufficiently far removed from the thioether group as not to mask or adversely affect the action of the thioether structure. Likewise, the thioethers remain essentially di-alkyl thioether, even though aryl or other nonaliphatic radicals be attached to the alkyl chain at a point remote from the thioether group, and such compounds may be utilized in the combination herein disclosed.

The thioethers utilized herein may be prepared by methods known in the art. For example, a mono-halogenated hydrocarbon may be reacted with a mercaptide to yield a thioether according to the reaction



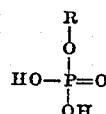
The conditions for carrying out this reaction are well known and alternative processes for forming thioethers may be found by reference to the literature.

The second component or type of addition agent utilized in the compounded oils of this invention comprises an activator for the thioethers enumerated in the foregoing disclosure. The activator comprises either an acid ester of an acid

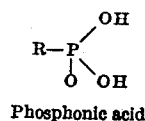
phosphorus, i. e. a partially esterified acid of phosphorus, or a salt of acids of phosphorus containing an organic substituent. Either the acid ester alone or the salt alone or mixtures of salts and acid esters may be used as an activator. These types of activators, when utilized in combination with the foregoing thioethers, give a synergetic effect and greatly enhance the oxidation inhibiting action of the thioethers. This is true even though the activator may not, when added alone, inhibit oxidation of the oil being stabilized.

Activators which may be added to hydrocarbon oil, such as mineral lubricating oil, to provide the second component of the new composition claimed herein preferably comprise metal salts of substituted oxy acids of phosphorus and/or acid esters of oxy acids of phosphorus, although corresponding compounds of the thio acids of phosphorus are not precluded. Salts of metals selected from groups II, III, IV and VI of Mendeleeff's Table of the Elements are preferred. Specific examples of such metals are aluminum, calcium, barium, strontium, chromium and magnesium. Salts of iron, cobalt, nickel, tin, zinc and lead comprise additional examples of compounds falling within the broader aspects of the invention. Likewise, ammonium salts of substituted acids of phosphorus containing an organic substituent are not precluded.

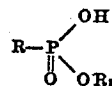
The salts of the substituted acids of phosphorus involved herein are preferably formed from substituted oxy acids of pentavalent phosphorus of the following type formula:



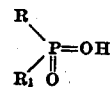
where R may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. Substituted phosphoric acids containing at least twelve carbon atoms are preferred, but where the salts are sufficiently soluble in oil, acids containing fewer carbon atoms may be utilized. Examples of preferred type acids are alkyl or alkaryl substituted phosphoric acids having at least twelve carbon atoms in the molecule. It is to be understood that the broader aspects of the invention include salts of other types of acids of phosphorus containing more than twelve carbon atoms. Additional examples of such substituted oxy acids of phosphorus are as follows:



Phosphonic acid



Monoester of phosphonic acid



Phosphinic acid

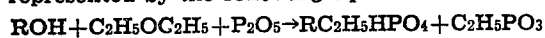
In all of the formulae R and R₁ may be alkyl,

aryl, alkaryl, aralkyl or cyclic non-benzenoid groups which, in turn, may be pure hydrocarbon constituents or oxygenated hydrocarbons such as alcohols, ketones, esters and ethers, or hydrocarbons containing substituents such as halogens (chlorine, bromine, iodine), amino, or nitro groups. Likewise, R and R₁ may be an oil soluble heterocyclic constituent, for example, a radical containing a nitrogen ring.

In general, salts of substituted derivatives of acids of phosphorus, such as phosphorous acid, H₃PO₃; hypophosphoric acid, H₂PO₃; orthophosphoric acid, H₃PO₄; pyrophosphoric acid, H₄P₂O₇ and the sulfur analogues of these acids fall within the broadest aspects of the invention. By "acids of phosphorus containing an organic substituent, or by "substituted acids of phosphorus" wherever used herein it is intended to designate acids of phosphorous containing an organic group of the types previously listed. The organic groups may be either directly attached to the phosphorus atom of the compound or attached thereto through an intervening atom, such as oxygen or sulfur. The term "oxy acids of phosphorus" is used to designate throughout the specification and claims acids of phosphorus in which only an oxygen atom may intervene between the hydrogen and phosphorus atoms of the parent acid.

The preferred acids are mono-esters of orthophosphoric acids or mixtures containing the mono-ester and the preferred salts comprise the aluminum, calcium, barium, magnesium and chromium salts of these acids. Examples of such salts are aluminum lauryl phosphate, aluminum cetyl phosphate, aluminum octadecyl phosphate, aluminum oleyl phosphate, aluminum (cetyl phenyl) phosphate, aluminum (di-amyl phenyl) phosphate, aluminum naphthenyl phosphate; calcium lauryl phosphate, calcium cetyl phosphate, calcium octadecyl phosphate, calcium oleyl phosphate, calcium (cetyl phenyl) phosphate, calcium (di-amyl phenyl) phosphate, calcium naphthenyl phosphate; barium lauryl phosphate, barium cetyl phosphate, barium octadecyl phosphate, barium oleyl phosphate, barium (cetyl phenyl) phosphate, barium (di-amyl phenyl) phosphate, barium naphthenyl phosphate; magnesium lauryl phosphate, magnesium cetyl phosphate, magnesium octadecyl phosphate, magnesium oleyl phosphate, magnesium (cetyl phenyl) phosphate, magnesium (di-amyl phenyl) phosphate, magnesium naphthenyl phosphate; chromium lauryl phosphate, chromium cetyl phosphate, chromium octadecyl phosphate, chromium oleyl phosphate, chromium (cetyl phenyl) phosphate, chromium (di-amyl phenyl) phosphate and chromium naphthenyl phosphate.

The substituted acids of phosphorus utilized in the present invention may be prepared by methods known in the art. For example, a mixture of a higher alcohol and phosphorus pentoxide in ethyl ether may be refluxed for several hours. The reaction by which the substituted phosphoric acid is formed in this process is believed to be represented by the following equation:



where R is an alkyl radical. The alkyl ethyl phosphoric acid is soluble in ether, while the ethyl metaphosphate is not, and the ether solution of the former may be separated from the latter by decantation. In preparing the metal salts herein involved, the ethyl group in the ethyl phosphoric acid above mentioned may be hydrolyzed to form the metal salt of the mono-alkyl orthophosphoric acid, i. e., the salt of RH₂PO₄. This type of proc-

ess is not limited to the alkyl derivatives but includes aryl ethyl phosphoric acid, alkaryl ethyl phosphoric acid, aralkyl ethyl phosphoric acid and ethyl phosphoric acids containing a cyclic non-benzenoid group.

The metal salts of the various substituted oxy acids of phosphorus may be conveniently prepared by reacting the acid with sodium hydroxide or potassium hydroxide and then precipitating the desired metal salt from a solution of the sodium or potassium salt by the addition of the appropriate metal ion. The salt also may be prepared by the direct neutralization of the acid, as, for example, with lime where the calcium salt is to be obtained. The calcium salt may also be prepared in a non-aqueous environment by the reaction of calcium carbide with the free substituted acid of phosphorus.

As has been previously pointed out, the present invention embraces the discovery that the combination of a thioether and an activator therefor imparts to hydrocarbon oils greatly enhanced stability against oxidation and gives a synergetic effect. The following data illustrate the synergetic action of thioethers and salts of substituted acids of phosphorus in hydrocarbon oils:

TABLE I
Oxidator data

Oil	C. c. oxygen absorbed at 300° F.		
	2 hrs.	4 hrs.	6 hrs.
White oil.....	Greater than 1,000 c. c. first ½ hr.		
White oil+1% cetyl ethyl thioether.....	Do.		
White oil+1% calcium cetyl phosphate.....	Do.		
White oil+1% calcium cetyl phosphate+0.25% cetyl ethyl thioether.....	50	69	88
White oil+1% di-octyl thioether.....	360		
White oil+1% di-octyl thioether+1% calcium cetyl phosphate.....	40		
White oil+2% cetyl methyl thioether.....	650 c. c. first hour.		
White oil+2% cetyl methyl thioether+1% calcium cetyl phosphate.....	10	15	

The above oxidator test is used for judging the oxidation susceptibility of an oil at elevated temperatures. The results are given in number of c. c. of oxygen absorbed by one hundred grams of oil. The temperature of this series of tests was 300° F. Specifically, the test is carried out by placing a weighted amount of oil in an oxygen absorption cell. The oil is completely saturated with oxygen by maintaining a foam with bubbles formed at a perforated glass surface in the cell. Constant temperature is maintained by an oil bath in which the cell and the intake line for the oxygen supply are immersed. Oxygen is circulated by means of a leakless oil-free pump and is preheated to bath temperature, passed through the oil in intimate contact therewith by means of the perforated glass surface and certain volatile oxidation products carried out with the gas stream are condensed in a water-cooled column and returned to the oil. The procedure of taking measurements consists in placing the weighed amount of oil in the cell as previously stated, evacuating the apparatus, filling with oxygen at atmospheric pressure and then accurately determining the decrease in the volume of oxygen caused by its absorption in the oil by the measurement of the oxygen volume in the system at the stated intervals during the test.

Additional oxidator data on combinations of other thioethers and an activator therefor are given in Table II.

TABLE II

Oil	C. c. O ₂ absorbed at 340° F. ¹		
	2 hrs.	4 hrs.	6 hrs.
White oil.....	Greater than 1,000 c. c. 1st ½ hr.		
White oil+1% calcium cetyl phosphate.....	Do.		
White oil+2% dioctadecyl thioether.....	>2,400		
White oil+2% dioctadecyl thioether+1% calcium cetyl phosphate.....	107	168	237
White oil+1% ethane dioctyl thioether.....	360		
White oil+1% ethane dioctyl thioether+1% calcium cetyl phosphate.....	45		
Highly refined naphthenic base oil.....	Greater than 1,000 c. c. 1st ½ hr.		
Highly refined naphthenic base oil+1% dilauryl thioether.....	100	296	538
Highly refined naphthenic base oil+1% dilauryl thioether+1% calcium cetyl phosphate.....	12	24	53
Highly refined naphthenic base oil+2% dicetyl thioether.....	50	>1,000	
Highly refined naphthenic base oil+2% dicetyl thioether+1% calcium cetyl phosphate.....	70	135	200

¹ Results given in number c. c. per 100 grams oil.

An additional indication of the novel cooperative action of thioethers and salts of substituted acids of phosphorus comprises the reduction in corrosion of copper-lead and cadmium-silver bearing metal alloys at elevated temperatures. Table III exemplifies this new result:

TABLE III

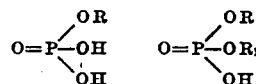
Oil	300° F. corrosion test	
	Loss Cu-Pb mg. weight 72 hrs.	Loss Cd-Ag mg. weight 72 hrs.
White oil.....	58	83
White oil+1% calcium cetyl phosphate.....	128	147
White oil+1% cetyl ethyl sulfide.....	41	0.4
White oil+1% cetyl ethyl sulfide+1% calcium cetyl phosphate.....	25	2.9

The above corrosion tests were carried out in the following manner. Glass tubes 2 inches in diameter and 20 inches long were immersed in an oil bath, the temperature of which was automatically controlled to within $\pm 1^\circ$ of the 300° F. test temperature. Approximately 300 c. c. of oil under test was placed in each tube and air was bubbled through it at the rate of 10 liters per hour. Strips of the different types of bearing metals were placed in the oil; in most cases the copper-lead and cadmium-silver bearing alloys were tested simultaneously in the same sample of oil. The weight loss of each strip was recorded. Before weighing, each strip was washed in petroleum ether and carefully wiped with a soft cotton cloth. The duration of the test was 72 hours.

It has also been observed that the thioether increases the efficiency of the substituted acids of phosphorus in stabilizing the hydrocarbon oil against the formation of gums or adhesive deposits on hot metal surfaces, for example, in the piston ring belt of internal combustion engines.

Mention has been made of acid esters of acids of phosphorus, i. e. partially esterified acids of phosphorus, as an activator for the thioethers. Examples of such acid esters are monocetyl orthophosphoric acid and dicetyl ortho phos-

phoric acid exemplifying respectively acids of the type formula



in which R and R₁ may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. The activating effect of acid esters of acids of phosphorus is illustrated by the following data:

TABLE IV
Oxidator data

Oil	C. c. O ₂ absorbed at 340° F. ¹	
	1 hr.	2 hrs.
White oil.....	Greater than 1,000 c. c. 1st ½ hr.	
White oil+1% cetyl ethyl thioether.....	Do.	
White oil+1% dicetyl phosphoric acid.....	Do.	
White oil+1% dicetyl phosphoric acid+1% cetyl ethyl thioether.....	10	15
White oil+1% monocetyl phosphoric acid.....	Greater than 1,000 c. c. 1st ½ hr.	
White oil+1% monocetyl phosphoric acid+1% cetyl ethyl thioether.....	125	290

¹ Results given in number c. c. per 100 grams oil.

The compounded lubricant herein disclosed may have one or more advantages, depending upon the particular compounds selected, the proportions utilized and the environment which the lubricating oil is to encounter. It should be observed, for example, that even though a compounded oil may be somewhat corrosive to copper-lead or cadmium-silver bearing alloys, Babbitt bearings are little, if at all, affected by such corrosive action. Hence, combinations of compounding agents which may not be particularly desirable for lubrication of copper-lead or cadmium-silver bearings at high temperatures where corrosion becomes a factor of importance may be highly useful and extremely advantageous in conjunction with the operation of internal combustion engines having bearings of Babbitt or other corrosive-resistant bearing metals. Likewise, combinations of compounding agents which may not be sufficiently powerful to stabilize a particular oil stock against oxidation under the most severe conditions may, none the less, be highly advantageous in such oils where the environment to be encountered is not so severe as, for example, in turbine oils, cable oils, electric switch oils, transformer oils, and the like. The present invention in its broader aspects is, therefore, not limited to the particular combination of ingredients giving the greatest stability or having all of the advantages of the preferred agents. The invention embraces various of the less advantageous combinations of addition agents which may find utility in particular applications where all possible improvements in properties of the oil may not be required or where the standard of performance may not be so high.

The compounding ingredients of this invention appear at present to find their greatest utility in highly refined or highly paraffinic mineral lubricating oil stocks, which stocks have heretofore been the most difficult to stabilize. However, it is to be understood that the invention is not limited to any particular base stock. The advantages herein disclosed may be obtained with various oil stocks, the selection of which will be determined by conditions and services which the

compounded lubricant is to encounter. The combination of compounding ingredients has been found useful, not only in Pennsylvania oils or highly refined naphthenic base oils, but also in moderately refined naphthenic base oils or in lubricating oils from Mid-Continent stocks as well as synthetic hydrocarbon oils such as hydrogenated polymers of olefin hydrocarbons.

The proportion of activator which may be added to hydrocarbon oils according to the principles of this invention may vary widely, depending on the uses involved and the properties desired. As little as 0.05% by weight of the activator gives measurable improvements, particularly as respects the color stability of the compounded oil. From approximately 0.25 to 2% of the salts of substituted acids of phosphorus or of the acid esters of acids of phosphorus may be added to lubricate containing thioethers where stability at high temperature comprises the principal property desired. More than 2% of these activators in mineral oils is not precluded. In general, however, more than 5% will be found unnecessary. The proportion of the thioethers present in the compounded oil may likewise vary widely, depending on the uses involved and the properties desired. As little as 0.05% of the thioether gives measurable improvement, although from approximately 0.1% to 2% is preferred where the compounded oil is to be used as a crankcase lubricant for internal combustion engines. 5% or more by weight of the thioethers may be dissolved in mineral oil or other suitable organic solvents for the purpose of preparing a concentrate capable of dilution with lubricating oils and the like. Concentrates containing high percentages, e. g. 50%, of the thioether and the activator comprise a convenient method of handling these ingredients and may be used as addition agents for lubricants in general, as well as for other purposes.

The combination of ingredients of this invention may be added to hydrocarbon oils containing other compounding agents, such as pour point depressants, oiliness agents, extreme pressure addition agents, blooming agents, and compounds for enhancing the viscosity index of the hydrocarbon oil. The invention in its broader aspects embraces hydrocarbon oils containing, in addition to the thioethers and activator, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form grease, as in the case of mineral castor machine oils or other compounded liquid lubricants.

As previously indicated, di-alkyl thioethers are highly susceptible to activation according to this invention. The invention in its broader aspects includes the substitution for the di-alkyl thioethers of cycloalkyl thioethers such as di-(cetyl-cyclohexyl) thioether, or mixed acyclic cycloalkyl thioethers like cetyl-cyclohexyl cetyl thioether or non-benzenoid cyclic thioethers of the thiophane type such as cetyl thiophane.

While the character of the invention has been described in detail and numerous examples of the combination given, this has been done by way of illustration only and with the intention that no limitation should be imposed on the invention thereby. Numerous modifications and variations of the illustrative examples may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

1. A composition comprising a hydrocarbon oil, a high molecular weight dialkyl thioether oxida-

tion inhibitor, and an activator for said thioether comprising a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient to enhance the action of said oxidation inhibitor.

2. A composition comprising a hydrocarbon oil, an oxidation-inhibiting amount of a high molecular weight dialkyl thioether containing at least one long carbon chain, and an activator for said thioether comprising a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to enhance the anti-oxidant action of said thioether.

3. A composition comprising a hydrocarbon oil, an oxidation-inhibiting amount of a high molecular weight dialkyl thiodiether containing at least one long carbon chain, and an activator for said thiodiether comprising a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to enhance the antioxidant action of said thiodiether.

4. A composition comprising a hydrocarbon oil, an oxidation-inhibiting amount of a high molecular weight dialkyl monothioether containing at least one long carbon chain, and an activator for said monothioether comprising a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to enhance the antioxidant action of said monothioether.

5. A composition comprising a hydrocarbon oil, an oxidation-inhibiting amount of a high molecular weight dialkyl dithiodiether containing at least one long carbon chain, and an activator for said dithiodiether comprising a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to enhance the antioxidant action of said dithiodiether.

6. A composition comprising a hydrocarbon lubricating oil, an oxidation-inhibiting amount of a thioether of the type formula:



where R and R₁ are alkyl radicals, at least one of which contains more than about ten carbon atoms and the sum of the number of carbon atoms in R and R₁ is at least about twelve, said oil also containing a small amount of a metal salt of an acid of phosphorus containing an organic substituent.

7. A composition comprising a hydrocarbon lubricating oil, an oxidation-inhibiting amount of a thioether of the type formula:



where R and R₁ are alkyl radicals, at least one of which contains more than about ten carbon atoms and the sum of the number of carbon atoms in R and R₁ is at least about twelve, said oil also containing at least about 0.05% of a metal salt of an acid of phosphorus containing an organic substituent.

8. A composition comprising a hydrocarbon oil solution containing at least about 0.05% of a high molecular weight dialkyl monothioether and at least about 0.05% of a polyvalent metal salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

9. A composition comprising a hydrocarbon oil solution containing at least about 0.05% of a high molecular weight dialkyl monothioether and at least about 0.05% of an alkaline earth metal salt

of an oxyacid of pentavalent phosphorus containing an organic substituent.

10. A composition comprising a hydrocarbon oil solution containing at least about 0.05% of a high molecular weight dialkyl monothioether and at least about 0.05% of a calcium salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

11. A composition comprising a hydrocarbon oil solution containing at least about 0.05% of a high molecular weight dialkyl monothioether and at least about 0.05% of a chromium salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

12. A composition comprising a hydrocarbon oil, a high molecular weight dialkyl thioether antioxidant for the oil and an activator for said thioether comprising an acid ester of an acid of phosphorus in an amount sufficient substantially to enhance antioxidant action of said thioether.

13. A composition comprising a mineral lubricating oil, from approximately 0.1% to 5% of a high molecular weight dialkyl monothioether, and from approximately 0.1% to 5% of a polyvalent metal salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

14. A process of stabilizing hydrocarbon oil subject to deterioration at elevated temperatures which comprise incorporating in said oil a small amount of a high molecular weight dialkyl thioether antioxidant and enhancing the effectiveness of said antioxidant by incorporating a small amount of an activator therefor.

15. A process of stabilizing hydrocarbon oil subject to deterioration at elevated temperatures which comprise incorporating in said oil a small amount of a high molecular weight dialkyl thioether antioxidant and enhancing the effectiveness of said antioxidant by incorporating a small amount of an activator therefor comprising an acid ester of an acid of phosphorus.

16. A process of stabilizing hydrocarbon oil subject to deterioration at elevated temperatures which comprise incorporating in said oil a small amount of a high molecular weight dialkyl thioether antioxidant and enhancing the effective-

ness of said antioxidant by incorporating a small amount of an activator therefor comprising a salt of an acid of phosphorus containing an organic substituent.

17. A process of stabilizing a viscous hydrocarbon oil which comprises incorporating in said oil a high molecular weight dialkyl thioether in an amount sufficient substantially to inhibit deterioration of the oil at elevated temperatures and enhancing the effectiveness of said thioether by incorporating in the oil a small amount of a polyvalent metal salt of an acid of phosphorus containing an organic substituent.

18. A stabilizer for hydrocarbon oils subject to deterioration by oxidation, said stabilizer comprising a high molecular weight dialkyl thioether antioxidant and a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient to enhance the antioxidant action of the thioether.

19. A stabilizer as defined in claim 18, further characterized in that said salt is a polyvalent metal salt of an oxyacid of pentavalent phosphorus.

20. A stabilizer as defined in claim 18, further characterized in that it comprises a concentrated hydrocarbon oil solution of said antioxidant and said salt.

21. A stabilizer for hydrocarbon oils subject to deterioration by oxidation, said stabilizer comprising a high molecular weight dialkyl thioether antioxidant and an acid ester of an acid of phosphorus, said ester being present in an amount sufficient to enhance the antioxidant action of the thioether.

22. A composition comprising a hydrocarbon oil, a high molecular weight dialkyl thioether antioxidant for said oil, and an activator for said thioether capable of enhancing the antioxidant action thereof and selected from the class consisting of the esters and salts of phosphoric acid, said activator being present in an amount sufficient to effect said enhancement.

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PAUL C. CONDIT.

Certificate of Correction

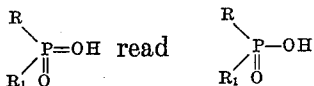
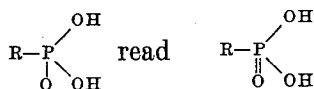
Patent No. 2,346,153.

April 11, 1944.

GEORGE H. DENISON, JR., ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 60, for

lines 69-73, for



page 3, first column, line 13, for "pyrophoric" read *pyrophosphoric*; line 19, for "phosphorous" read *phosphorus*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of July, A. D. 1944.

[SEAL]

LESLIE FRAZER,
Acting Commissioner of Patents.

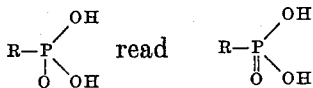
Certificate of Correction

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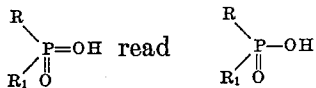
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