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COMPOUNDED HYDROCARBON OIL

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This invention relates to a new and useful composition of matter comprising a stabilized hydrocarbon oil. More particularly, the invention relates to viscous hydrocarbon oils containing a new combination of stabilizing agents.

The production of improved hydrocarbon oils, and particularly of lubricating oils having desired characteristics, has been the subject of extensive research and investigation. Generally speaking, the compounding of hydrocarbon oils to obtain desired characteristics involves empirical phenomena, and the action of untested combinations of different types of compounding agents cannot be predicted. It has been found that even tested combinations of different types of compounding agents behave differently in different types of lubricating oil bases.

A characteristic which has been found particularly significant is the tendency of hydrocarbon oils to deteriorate or partially decompose and oxidize when subjected to high temperatures. This deterioration is evidenced by the deposition of adhesive deposits on hot metal surfaces over which the hydrocarbon oil may flow. It is important that resistance to such deterioration be imparted to hydrocarbon oils, particularly to lubricating oils, in order that such compositions may be relatively free from the tendency to form such deposits even under high temperatures and severe operating conditions. A direct result of this type of deterioration during lubrication of internal combustion engines, such as engines of the Diesel type, is the tendency of the oil to cause or permit the sticking of piston rings.

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 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 deterioration by heat and oxidation at high temperature levels in the order of those above mentioned.

One means of stabilizing hydrocarbon lubricating oils which has been quite successful comprises incorporation in the hydrocarbon oil of both a metal phenate and a salt of a substituted acid of phosphorus containing an organic constituent. These two types of compounding agents cooperate to impart a number of highly desirable properties to the oil. However, some difficulty has been encountered in the use of this combination of stabilizers in that various oil stocks are not so responsive to stabilization with the combination of addition agents as would be desirable. The stabilizers work excellently in

many oils, such as oils of moderate refinement and particularly acid refined naphthenic base or Western oils, but seem not to improve highly refined or highly paraffinic lubricating oils sufficiently to meet the rigid requirements of certain lubrication problems such as encountered in the lubrication of the pistons and piston rings of engines of the Diesel type.

In general, it may be said that highly paraffinic or highly refined hydrocarbon lubricating oils respond to stabilization with a combination of metal phenates and salts of substituted acids of phosphorus in a manner inferior to less highly refined hydrocarbon lubricating oils. By "highly paraffinic lubricating oils" it is intended to designate oils obtained from Pennsylvania crudes and other paraffinic crudes or synthetically prepared paraffinic type oils which are characterized by a viscosity index superior to that of the naphthenic base type oils. The term "highly refined lubricating oils" is intended to designate oils which have been subjected to a high degree of refinement with, for example, selective solvents or sulfuric acid in a manner well known in the art. These highly paraffinic or highly refined hydrocarbon lubricating oils demand a premium and have many highly advantageous properties. They do have disadvantages, among which are an inferior response to stabilization with compounding agents and corrosivity to various new bearing materials.

Among the above-mentioned new bearing materials are binary and ternary alloys of cadmium and copper; for example, cadmium-silver-copper, cadmium-nickel-copper, and copper-lead-nickel are in use. Under the conditions imposed by modern engineering design, these new alloy bearings are commonly subjected to more severe operating conditions than were usual in the older art. It has been found that in actual use under these conditions there often develops serious destructive action on the bearing surface by paraffinic or highly refined lubricating oils. Compounding agents which may stabilize these oils against gum formation and the deposition of adhesive deposits have, in general, not satisfactorily prevented this corrosive action of highly refined or highly paraffinic oils when added thereto.

An object of the invention is to improve the responsiveness of hydrocarbon oils to stabilization with metal phenates and salts of substituted acids of phosphorus. Other objects and advantages of the invention will be apparent from the following description and disclosure.

The invention provides a combination of compounding agents capable of imparting to highly paraffinic and/or highly refined oils great stability against oxidation or deterioration at temperatures of even 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 highly paraffinic or highly refined lubricating oils, as previously described. It has been discovered that incorporation of a sensitizer of the thioether type, such as dialkyl thioether, in hydrocarbon oils improves the responsiveness of the oil to stabilization with anti-piston ring sticking agents, such as metal phenates and salts of substituted acids of phosphorus. Thioethers may be utilized according to the invention to sensitize or improve the responsiveness of highly refined or highly paraffinic oils to stabilization with metal phenates and salts of substituted acids of phosphorus. However, the invention is not limited to the improvement of these particular base stocks. The thioethers may likewise be incorporated in oils of moderate or little refinement or in Mid-Continent or naphthenic base oils to enhance responsiveness of these oils to stabilization with said compounding agents.

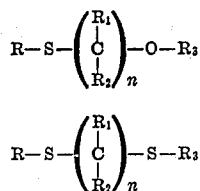
Examples of sensitizers operative for the purpose of the invention are high molecular weight dialkyl thioethers containing at least one long carbon chain. By "long carbon chain" is meant a radical containing at least approximately eight carbon atoms. By "high molecular weight thioethers" it is intended to designate thioethers containing in the order of a total of twelve or more carbon atoms. Examples of such high molecular weight dialkyl thioethers are the following: dioctyl monothioether, octyl decyl monothioether, octyl dodecyl monothioether, octyl tetradecyl monothioether, octyl cetyl monothioether, didecyl monothioether, decyl dodecyl monothioether, decyl tetradecyl monothioether, decyl cetyl monothioether, didodecyl monothioether, dodecyl tetradecyl monothioether, dodecyl cetyl monothioether, ditetradecyl monothioether, tetradecyl cetyl monothioether, dicetyl monothioether, dioctadecyl thioether. The preferred dialkyl monothioethers contain one long chain and one short chain, for example, dodecyl methyl monothioether, dodecyl ethyl monothioether, dodecyl propyl monothioether; tetradecyl methyl monothioether, tetradecyl ethyl monothioether, tetradecyl propyl monothioether; cetyl methyl monothioether, cetyl ethyl monothioether, cetyl propyl monothioether.

The above compounds are represented by the type formula:



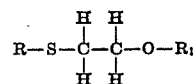
where R and R₁ may be the same or different alkyl radicals. R and R₁ may be either a straight hydrocarbon chain or a branched chain such as obtained from isobutylene polymers or interpolymers of butylene with isobutylene and other analogous olefin polymer derivatives.

Monothio or dithio dialkyl diethers of the general formulae:

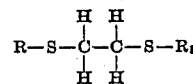


for example, monothioethane dialkyl diethers or dithioethane dialkyl diethers, are also effective in

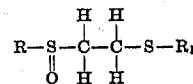
the combination of this invention. These latter compounds may be represented by the formulae:



and

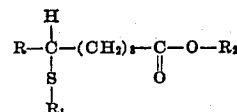


where R and R₁ may be any of the alkyl radicals previously listed above for these radicals, R₂ and R₃ may be either hydrogen or any one of such alkyl radicals, and n may be any whole number. Likewise sulfoxides such as



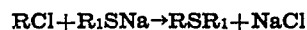
are not precluded.

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 the 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:

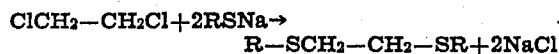


where R, R₁ and R₂ are alkyl radicals, R₁ preferably being a relatively short chain such as an ethyl group. The carbonyl group of the above type compound is sufficiently far removed from the thioether group as not to mask or adversely affect the action of the thioether structure. Likewise, the thioethers remain essentially dialkyl thioether, even though aryl or other non-alkyl 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:

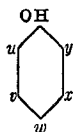


The conditions for carrying out this reaction are well known, and alternative processes for forming thioethers may be found by reference to the literature. The di-thio-ethane di-ethers may be prepared from ethylene dichloride by the reaction:



Metal phenates which may be added to hydrocarbon oils to provide an anti-piston ring sticking component of the new composition of matter of this invention comprise the alkali, alkaline earth and other metal phenates. Examples of such metal phenates are: sodium phenates, potassium phenates, beryllium phenates, calcium

phenates, strontium phenates, barium phenates, magnesium phenates, zinc phenates, cadmium phenates and aluminum phenates. The metal phenates are preferably formed from high molecular weight phenols of the type formula:



in which *u*, *v*, *w*, *x* and *y* are selected from the group consisting of hydrogen, hydrocarbon, oxy and hydroxy radicals. The phenol preferably contains at least one alkyl group having more than four carbon atoms. The term "hydrocarbon radicals" used in the above connection is intended to include alkyl, aryl, alkaryl, aralkyl and cyclic non-benzenoid groups; and the term "oxy radicals" refers to a group in which the hydrogen of a hydroxy radical has been replaced by esterification, neutralization or the like. Although phenols containing at least one alkyl substituent are preferred, the invention does not preclude compounds containing no alkyl groups and embodies the substitution of aryl, alkaryl, aralkyl and cyclic non-benzenoid groups, as well as conjugated rings in the aromatic nucleus to which the phenolic hydroxy group is directly attached. Likewise, the phenolic radical may contain oxygenated hydrocarbon groups, such as alcohols, ketones, esters and ethers, or the phenolic radical may contain substituents such as halogens (chlorine, bromine, iodine), amino or nitro groups either in the ring or in a substituent of the ring. Further, the phenols may contain a heterocyclic substituent, for example, a radical containing a nitrogen ring.

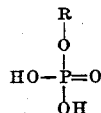
Examples of specific metal phenates which may be utilized comprise: sodium lauryl phenate, sodium cetyl phenate, calcium lauryl phenate, calcium cetyl phenate, calcium di(amyl) phenate, calcium heptyl phenate, calcium p-tertiary amyl phenate, calcium monochloramyl phenate, calcium p-cyclo-hexanol phenate, aluminum lauryl phenate, aluminum cetyl phenate, aluminum dicetyl phenate, magnesium cetyl phenate, barium cetyl phenate, and calcium cetyl cresylate.

The metal phenates of this invention may be prepared by any suitable method. For example, the alkyl phenols may be obtained by alkylation of the phenols with an olefin or an olefin polymer, such as di-, tri- and tetra-butylenes or di-, tri- and tetra-isobutylenes in the presence of a suitable catalyst, such as sulfuric acid. The alkylated phenol may then be reacted with the proper metal or metal ion, or the alkylated phenol may be converted to a sodium salt and the salt reacted with other appropriate metal ions to form other desired salts. The preparation of the metal phenates comprises no part of this invention and may be effected by those skilled in the art without undue difficulties.

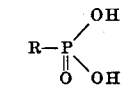
Salts of substituted acids of phosphorus which may be added to hydrocarbon oils to provide a third component of the new composition preferably comprise metal salts of substituted oxyacids of phosphorus, although metal salts of substituted thioacids of phosphorus are not precluded. Salts of metals selected 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.

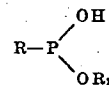
The salts of the substituted acids of phosphorus involved herein are preferably formed from substituted oxyacids of pentavalent phosphorus of the following type formula:



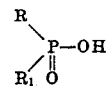
where R may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. Substituted phosphoric acids containing at least twelve carbon atoms are preferred but, where the salts are sufficiently soluble in oil, acids containing fewer carbon atoms may be utilized. Examples of preferred type acids 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 oxyacids of phosphorus are as follows:



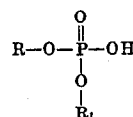
Phosphonic acid



Monoester of phosphonic acid



Phosphinic acid



Diester of phosphoric acid

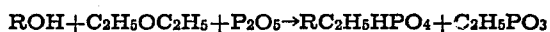
In all of the formulae R and R₁ may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid groups which, in turn, may be pure hydrocarbon constituents or oxygenated hydrocarbons such as alcohols, ketones, esters and ethers, or hydrocarbons containing substituents such as halogens (chlorine, bromine, 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 phosphorus 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 "oxyacids 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 substituted orthophosphoric acids 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 (diamyl phenyl) phosphate, aluminum naphthenyl phosphate; calcium lauryl phosphate, calcium cetyl phosphate, calcium octadecyl phosphate, calcium oleyl phosphate, calcium (cetyl phenyl) phosphate, calcium (diamyl phenyl) phosphate, calcium naphthenyl phosphate; barium lauryl phosphate, barium cetyl phosphate, barium octadecyl phosphate, barium oleyl phosphate, barium (cetyl phenyl) phosphate, barium (diamyl phenyl) phosphate, barium naphthenyl phosphate; magnesium lauryl phosphate, magnesium cetyl phosphate, magnesium octadecyl phosphate, magnesium oleyl phosphate, magnesium (cetyl phenyl) phosphate, magnesium (diamyl phenyl) phosphate, magnesium naphthenyl phosphate; chromium lauryl phosphate, chromium cetyl phosphate, chromium octadecyl phosphate, chromium oleyl phosphate, chromium (cetyl phenyl) phosphate, chromium (diamyl 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 monoalkyl orthophosphoric acid, i. e. the sale of RH_2PO_4 . This type of process 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 oxyacids of phosphorus may be conveniently prepared by reacting the acid with sodium hydroxide or potassium hydroxide and then precipitating the desired metal salt from the 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.

The metal phenate and salt of substituted acids of phosphorus cooperate in lubricating oil to yield new and unpredictable advantages. For example,

these two components in combination are more efficient in maintaining piston cleanliness and inhibiting piston ring sticking than is an oil containing either of the components alone for the reason that the metal phenates permit the formation of an orange-colored gum on the lower portion of pistons of Diesel engines after short periods of operation, and the salt of substituted acids of phosphorus permits slight thermal decomposition and some deposition of carbon in the top piston ring grooves of such engines under severe operating conditions. These two ingredients in combination inhibit both formation of gum on the piston skirt and deposition of carbon in the piston ring grooves. Also, the salt of substituted acids of phosphorus tends to form black deposits when contacted with metal surfaces at 425° F. or above. The metal phenate prevents such deposits up to temperatures as high as 550° F. Further, by this combination of inhibitors an increased stability of the oil solution of each of the components is obtained. The manner in which the metal phenate and the salts of substituted acids of phosphorus cooperate is more fully set forth in the application of George L. Neely et al., Serial No. 242,292, filed November 25, 1938, for Compounded mineral oil, granted January 14, 1941, as United States Letters Patent No. 2,228,671.

The sensitizers disclosed herein enhance the above cooperative effect of the phosphate and phenate combination and enable the phosphate-phenate combination to impart very high stability to all hydrocarbon oils. In some instances, the phenate-phosphate combination is unable to impart sufficient stability to particular hydrocarbon oil stocks, without introducing undesirable properties, to meet the exacting requirements of some lubricating oil services as, for example, in Diesel engines. The sensitizer when added to such base oils so increases the responsiveness of these oils to the stabilizing action of the metal phenate and salts of substituted acids of phosphorus that these requirements may be satisfied.

The following data illustrate the effectiveness of sensitizers of the dialkyl thioether type to enhance the responsiveness of hydrocarbon oils to stabilization with metal phenates and salts of substituted acids of phosphorus:

TABLE I
Oxidator data

Oil	Cc. oxygen absorbed at 340° F.		
	2 hrs.	4 hrs.	6 hrs.
White oil.....	Greater than 1000 cc. 1st ½ hr.		
White oil+1% dicetyl thioether+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	60	70	80
Paraffinic base oil S. A. E. 30.....	100	200	-----
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	120	200	Above 750
Paraffinic base oil S. A. E. 30+1% dioctadecyl thioether+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	52	67	97
Mid-Continent base oil.....	210	346	-----
Mid-Continent base oil+1% dioctadecyl thioether.....	114	279	468
Mid-Continent base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	300	-----	-----
Mid-Continent base oil+1% dioctadecyl sulfide+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	86	110	180

The above oxidator test is used for judging the oxidation susceptibility of an oil at elevated temperatures. The results are given in number of

alloys at elevated temperatures by normally corrosive base oils. The data in Tables II and III exemplify this result:

TABLE II
Strip corrosion test—300° F.

	Copper-lead wt. loss, mg.			Increase in viscosity at 210° F.	Neutralization number
	24 hrs.	48 hrs.	72 hrs.		
White oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	19.0	45.0	53.4	10.6	1.34
White oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dicetyl thioether.....	1.5	1.3	1.0	4.0	.05
Mid-Continent base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	24.0	55.1	71.0	11.5	1.80
Mid-Continent base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dicetyl thioether.....	0.7	1.4	2.2	3.5	.18
Mid-Continent base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+2% cetyl ethyl thioether.....	2.4	1.9	2.5	5.6	.68
Mid-Continent base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% diheptadecyl thioether.....	11.9	35.2	47.6	4.6	.40
Solvent refined naphthenic base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	1.5	3.2	4.3	4.7	.49
Solvent refined naphthenic base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dicetyl thioether.....	+0.8	+0.6	0.5	4.4	.45
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	1.3	17.7	37.7	2.0	-----
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dicetyl thioether.....	0.0	2.2	14.6	2.1	.37
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+25% cetyl ethyl thioether.....	+0.4	4.0	18.6	1.2	.47
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+5% cetyl ethyl thioether.....	0.5	2.5	9.5	0.1	.25
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% cetyl ethyl thioether.....	0.0	0.7	1.4	0.5	.24
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	8.0	45.4	99.6	7.6	.79
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+25% dicetyl thioether.....	0.6	2.4	19.4	5.2	.35
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+5% dicetyl thioether.....	1.1	2.3	9.9	4.2	.24
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dicetyl thioether.....	0.5	0.8	2.6	4.0	.28
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+5% cetyl ethyl thioether.....	1.0	1.6	2.9	4.7	.27
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+2% cetyl ethyl thioether.....	+1.7	+2.1	+2.2	-----	.52
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+2% dicetyl thioether.....	0.9	1.2	2.3	2.2	.30
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+5% dilauryl thioether.....	+0.6	+0.4	3.3	4.7	.21
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dimethyl methane diamyl dithioether.....	0.6	1.1	4.1	5.6	.61
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+2% thioether from chlorinated kerosene hydrocarbons.....	0.8	1.2	1.1	3.7	.37
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% ethane diamyl dithioether.....	1.0	1.0	0.9	6.7	.49

¹ Darkened.

cc. of oxygen absorbed by one hundred grams of oil. The temperature of this series of tests was 340° 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 weighted 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.

An additional indication of the novel cooperative action of sensitizers of the thioether type with metal phenates and salts of substituted acids of phosphorus comprises the reduction in corrosion of copper-lead and cadmium-silver bearing metal

TABLE III
Strip corrosion test—300° F.

	Cadmium-silver mg. lost		
	24 hrs.	48 hrs.	72 hrs.
50 White oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	8	38	40
55 White oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dicetyl thioether.....	0.1	0.1	0.1
Paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	.2	19	110
60 Paraffinic base oil S. A. E. 30+1% dicetyl thioether+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	0	0	0
Mid-Continent base oil+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	.7	31	54
65 Mid-Continent base oil+1% dicetyl thioether+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate.....	0	0	0

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 cc. 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 tests was 72 hours.

Additional corrosion data are given in Table IV. These data were obtained in tests run at 325° F. in the presence of added copper as a catalyst.

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 such base stocks since advantages herein disclosed may be obtained with moderately refined or less paraffinic lubricating oils. Thus the combination of compounding ingredi-

TABLE IV
Strip corrosion test—325° F.

	Copper-lead wt. loss, mg.			Increase in viscosity at 210° F.	Neutralization number
	24 hrs.	48 hrs.	72 hrs.		
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate	44.7	111.1	177.8	8.6	.94
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% dioctyl thioether	10.9	15.1	17.6	9.9	1.10
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.3% calcium cetyl phenyl phosphate	37.8	89.8	135.0		0.69
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.3% calcium cetyl phenyl phosphate+25% cetyl ethyl thioether	14.1	31.8	48.9	7.8	1.27
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.3% calcium cetyl phenyl phosphate+.5% cetyl ethyl thioether	9.8	13.6	30.2	9.4	1.77
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.3% calcium cetyl phenyl phosphate+1% cetyl ethyl thioether	2.6	4.1	6.5	12.3	2.10
Solvent refined paraffinic base oil S. A. E. 30+0.5% calcium cetyl phenate+0.25% calcium cetyl phosphate+1% ethane dioctyl dithioether	16.2	11.9	21.1	9.0	.94

¹ Darkened.

The above data show that the sensitizers increase the efficiency of metal phenates and salts of substituted acids of phosphorus in stabilizing hydrocarbon oils against oxidation. The data also illustrate that the combination of addition agents herein disclosed permits the stabilization of normally corrosive lubricating oil stocks or lubricating oil stocks which become corrosive to copper-lead or cadmium-silver alloy type bearings without the attendant disadvantages heretofore encountered.

The compounded lubricant herein disclosed may have one or more advantages, depending upon the particular compounding agents 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 one particular type of bearing alloy other bearings may be little, if at all, affected by such corrosive action. Hence, combinations of compounding agents which may not be particularly desirable for lubrication where corrosion becomes a factor of importance may be highly useful and extremely advantageous in conjunction with the operation of internal combustion engines having corrosive-resistant bearing metals. Likewise, combinations of compounding agents which are not sufficiently powerful to stabilize a particular oil stock under the most extreme conditions may, none the less, be highly advantageous in such oils where the environment to be encountered is not so severe. The present invention, in its broader aspects, is therefore not limited to the particular combination of ingredients giving the greatest stability or passing all of the very severe tests hereinabove described. 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 proportion of sensitizers present in the compounded oil may vary widely, depending on the uses involved and the properties desired. As little as 0.05% of the thioether sensitizer gives measurable improvement, although from approximately 0.25% to 2% is preferred. Five per cent or more by weight of the thioether sensitizer may be dissolved in mineral oil or other suitable solvents for the purpose of preparing a concentrate capable of dilution with lubricating oils and the like.

The proportion of metal salts of substituted acids of phosphorus which may be added to hydrocarbon lubricating oils according to the principles of the present invention may also vary widely, depending upon the uses involved and the stability desired. As little as 0.05% by weight of the salts of substituted acids of phosphorus gives measurable improvement, particularly as respects the color stability of the compounded oil. From approximately 0.25% to 2% of the salts may be added where stability at high temperature comprises the principal property desired. More than 2% of the salts is not precluded. Similarly, the proportion of metal phenates depends on conditions which the lubricant is to encounter and the stability desired. Measurable improvement is obtained with 0.05% of the phenate, 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. As much as 50% or more by weight of the various phenates may be dissolved in the oil for the purpose of preparing a concentrate capable of dilution with the lubricating oils and the like. Concentrates containing high percentages of the thioether, the phenate and the salts of the sub-

stituted acids of phosphorus comprise a convenient method of handling these compounding agents, and the concentrate may be used as an addition agent for lubricants as well as for other purposes.

There is a preferred range of ratios between the amount of salts of substituted acids of phosphorus and the amount of metal phenates in the compounded oil where stability at high temperatures and ability to improve operation of internal combustion engines are the properties to be obtained. This range of ratios may vary from approximately two parts of the metal phenate to one part of the salts of substituted acids of phosphorus, on the one hand, to approximately five parts of the metal phenate and four parts of the salts of the substituted acids of phosphorus, on the other hand. This preferred ratio of these compounds is based on the relative amount of the two ingredients, irrespective of the total amount which may be in the oil.

The combination of ingredients of this invention may be utilized in turbine oils, cable oils, electric switch oils, transformer oils and the like. The combination of ingredients of this invention may also be added to hydrocarbon lubricating oils containing other compounding agents, such as pour point depressants, oiliness agents, extreme pressure addition agents, blooming agents, compounds for enhancing the viscosity index of the hydrocarbon oil, 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, dialkyl thioethers are highly susceptible to activation according to this invention. In its broader aspects the invention includes the substitution for the dialkyl 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 upon 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 containing a stabilizing amount of a metal phenate sufficient to inhibit deterioration of the oil and a polyvalent metal salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient to augment the stabilizing action of said metal phenate, and a thioether sensitizer for the hydrocarbon oil capable of enhancing its responsiveness to stabilization by said phenate and said salt.

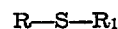
2. A composition comprising a hydrocarbon oil, a stabilizing amount of a metal phenate sufficient to inhibit deterioration of said oil, a salt of an acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient to augment the stabilizing action of said phenate, and a dialkyl thioether sensitizer in an amount sufficient to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of the metal phenate and said salt.

3. A composition as defined in claim 2, in which the sensitizer is a high molecular weight dialkyl thioether containing at least one long carbon chain.

4. A composition as defined in claim 2, in which the sensitizer is a high molecular weight dialkyl monothioether.

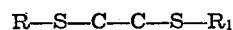
5. A composition as defined in claim 2, in which the sensitizer is a high molecular weight dialkyl dithiodiether.

6. A composition comprising a hydrocarbon lubricating oil, a sensitizer 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 small amounts of a metal phenate and a metal salt of an acid of phosphorus containing an organic substituent, the amount of said phenate being sufficient to inhibit deterioration of the oil, the amount of said metal salt of an acid of phosphorus being sufficient to augment the stabilizing action of said phenate, and the amount of said sensitizer being sufficient substantially to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of said phenate and said metal salt.

7. A composition comprising a hydrocarbon lubricating oil, a sensitizer of the type formula:



where R and R₁ are alkyl radicals, said oil also containing small amounts of a metal phenate and a metal salt of an acid of phosphorus containing an organic substituent, the amount of said phenate being sufficient to inhibit deterioration of the oil, the amount of said metal salt of an acid of phosphorus being sufficient to augment the stabilizing action of said phenate, and the amount of said sensitizer being sufficient substantially to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of said phenate and said metal salt.

8. A composition comprising a hydrocarbon oil solution of a dialkyl monothioether, an alkaline earth metal phenate, and an alkaline earth metal salt of an oxyacid of pentavalent phosphorus containing an organic substituent, the amount of said phenate being sufficient to inhibit deterioration of the oil, the amount of said alkaline earth metal salt of an acid of phosphorus being sufficient to augment the stabilizing action of said phenate, and the amount of said dialkyl monothioether being sufficient substantially to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of said phenate and said metal salt.

9. A composition comprising a hydrocarbon oil solution, from approximately 0.05% to approximately 2% by weight based on the oil of a dialkyl monothioether, from approximately 0.1% to approximately 2% by weight based on the oil of a polyvalent metal salt of a phenol containing more than ten carbon atoms, and from approximately 0.05% to approximately 2% by weight based on the oil of a polyvalent metal salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

10. A composition comprising a hydrocarbon oil solution, from approximately 0.05% to approximately 2% by weight based on the oil of a dialkyl monothioether, from approximately 0.1% to approximately 2% by weight based on

the oil of an alkaline earth metal salt of a phenol containing more than ten carbon atoms, and from approximately 0.05% to approximately 2% by weight based on the oil of a polyvalent metal salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

11. A composition comprising a hydrocarbon oil solution, from approximately 0.05% to approximately 2% by weight based on the oil of a dialkyl monothioether, from approximately 0.1% to approximately 2% by weight based on the oil of an alkaline earth metal salt of a phenol containing more than ten carbon atoms, and from approximately 0.05% to approximately 2% by weight based on the oil of an alkaline earth metal salt of an oxyacid of pentavalent phosphorus containing an organic substituent.

12. A process of stabilizing hydrocarbon oil subject to deterioration at elevated temperatures which comprises incorporating in said oil a small amount of a metal phenate and of a salt of an acid of phosphorus containing an organic substituent, and enhancing the responsiveness of the hydrocarbon oil to the potential stabilizing action of said metal phenate and said salt by incorporating in the oil from approximately 0.05% to 5% of a thioether sensitizing agent.

13. A process of simultaneously stabilizing a hydrocarbon oil selected from the group consisting of highly refined and highly paraffinic mineral oils and inhibiting corrosiveness of said oil to metal bearings of the cadmium-silver and copper-lead alloy type which comprises incorporating in said oil a small amount of a metal phenate and of a salt of an acid of phosphorus containing an organic substituent, and enhancing the responsiveness of the hydrocarbon oil to the potential stabilizing action of said metal phenate and said salt by incorporating in the oil from approximately 0.05% to 5% of a sensitizing agent of the dialkyl thioether type capable of inhibiting the corrosive action toward said bearing metals otherwise normally developed by said hydrocarbon oil during use.

14. A lubricating composition comprising a hydrocarbon oil containing a metal phenate in an amount sufficient to inhibit deterioration of the oil, a salt of an acid of phosphorus in an amount sufficient to augment the stabilizing

action of the phenate, and a thioether sensitizer in an amount sufficient substantially to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of the metal phenate and said salt.

15. A lubricating composition comprising a hydrocarbon oil containing a metal phenate in an amount sufficient to inhibit deterioration of the oil, a salt of an acid of phosphorus in an amount sufficient to augment the stabilizing action of the phenate, and a polythioether sensitizer in an amount sufficient substantially to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of the metal phenate and said salt.

16. A lubricating composition comprising a hydrocarbon oil containing a metal phenate in an amount sufficient to inhibit deterioration of the oil, a salt of an acid of phosphorus in an amount sufficient to augment the stabilizing action of the phenate, and a monothioether sensitizer in an amount sufficient substantially to enhance the responsiveness of the hydrocarbon oil to the stabilizing action of the metal phenate and said salt.

17. An addition agent for lubricating oils, capable of inhibiting deterioration of said oils, which comprises a concentrated organic solution of a metal phenate having an oil-solubilizing substituent in an aryl radical thereof, a metal salt of a substituted acid of phosphorus containing an organic substituent, and a thioether sensitizer for said phenate and salt, said concentrated solution containing more than 2% by weight based on the oil of said metal phenate, more than 2% by weight based on the oil of said metal salt, and more than 2% by weight based on the oil of said thioether sensitizer, said concentrated solution being capable of dilution with mineral lubricating oil to form a homogeneous mixture containing from approximately 0.05% to approximately 2% by weight of said phenate, from approximately 0.05% to approximately 2% by weight of said metal salt, and from approximately 0.05% to approximately 2% by weight of said thioether sensitizer.

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