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COMPOUNDED MINERAL OIL

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8 Claims. (Cl. 252—53)

This invention relates to a new and useful composition of matter and involves a composition comprising a hydrocarbon oil and a new combination of stabilizing ingredients. More particularly, the invention pertains to a viscous hydrocarbon oil containing a metal phenate and an oxidation inhibitor.

The production of improved hydrocarbon oils, and particularly of lubricating oils having desired characteristics, has been the subject of extensive research and investigation in recent years. 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.

A characteristic which has been the subject of extensive investigation 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.

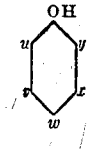
The crankcase lubricant in internal combustion engines is subjected to extremely severe operating conditions, and in engines of the Diesel type the lubricant encounters in the piston ring zone temperatures of from approximately 425° to 650° F. and pressures from the oxidizing combustion gases as high as 750 to 1150 pounds per square inch. In its more specific aspects the present invention is directed to the improvement of hydrocarbon lubricating oils by imparting thereto increased resistance to deterioration by heat at high temperature levels in the order of those above mentioned. It has been observed that high temperature oxidation inhibitors, i. e., oxidation inhibitors effective at temperatures as high as 300° F. or above, in combination with metal phenates, impart to hydrocarbon lubricating oils a number of highly desirable properties and improve the lubrication and operation of internal combustion engines. More particularly, it has been discovered that a lubricating oil containing both a metal phenate and a high temperature oxidation inhibitor permits longer periods of operation of engines without the necessity of major overhauls heretofore occasioned by stuck piston rings, wear of pistons and cylinder walls, or, in some instances, corrosion of bearing metal alloys.

The broader aspects of the invention involve the discovery that oxidation inhibitors in general and metal phenates in particular cooperate to give new results in hydrocarbon oil compositions. Hydrocarbon oils containing this combination of ingredients have greater stability under various operating conditions than do oils containing either of these types of ingredients alone. For example, the same stability is not obtainable with 1% of a metal salt of a phenol or with 1% of an anti-oxidant in a lubricating oil as is obtained with ¾% of the metal phenate and ¼% of the anti-oxidant in the same lubricating oil. Although it has been discovered that oxidation inhibitors in general cooperate with phenates in the above unpredictable manner, the mechanism of this cooperation has not been established and the inventors therefore refrain from any attempted explanation of the phenomena observed.

It should be noted that oxidation inhibitors or anti-oxidants which are effective at low temperatures to inhibit oxidation in hydrocarbon oils may not be effective at higher temperatures and under more severe operating conditions, such as those which lubricating oils encounter in the piston ring belt of Diesel engines. Although the broader aspects of the invention are not so limited it is preferred to utilize in combination with metal phenates, high temperature oxidation inhibitors effective above 300° F. and preferably effective to inhibit oxidation of lubricating oils containing metal phenates at temperatures in the range of 400° to 500° F.

Metal phenates, which may be added to hydrocarbon oils such as mineral lubricating oils to provide one component of the new composition of matter herein claimed, 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.

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-cyclohexanol phenate; aluminum lauryl phenate, aluminum di-cetyl 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, in the presence of sulfuric acid, with an olefine or an olefine polymer, such as di, tri and tetra butylenes or di, tri and tetra isobutylenes. The alkylated phenol may then be reacted with the proper metal or metal ion, or the sodium or potassium salts of the alkyl phenol may be reacted with the proper metal ion to obtain the desired salt. 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.

As has been previously indicated, the invention in its broad aspects embraces hydrocarbon oils containing, generically, anti-oxidants for hydrocarbon oils in combination with metal phenates. Many anti-oxidants for hydrocarbon oils are known, and the following types are mentioned for purposes of illustration:

1. Oil soluble hydroxy compounds, like polyhydroxy phenols, condensed ring phenols, alkyl substituted phenols, and naturally occurring inhibitors which may be extracted from fats and petroleum oils.

2. Nitrogen compounds comprising aryl-amines (di-amines, di-aryl-amines), nitroso-amines, cyclo-aliphatic-amines, and condensation products of aldehydes or ketones with aromatic amines.

3. Oxygenated organic compounds comprising aryl-ethers, aryl-ketones and alkyl ketones.

4. Esters of certain types of acids, namely, oil-soluble esters of alpha- and beta-hydroxy carboxylic acids in which a carboxyl group is not more than two carbon atoms removed from a hydroxy group, esters of poly-carboxylic acids having two carboxyl groups no more than two carbon atoms apart and esters of carboxylic acids having an unsaturated carbon-to-carbon bond conjugated with the carboxyl group.

5. Oil-soluble organo-metallic compounds of metals selected from Groups II, III, IV and V of Mendeleeff's Periodic Table.

6. Sulfur compounds (other than compounds in which the sulfur is in a carbocyclic ring), such as aryl mercaptans, sulfides, di-sulfides, poly-sulfides, aryl-thio-esters, alkyl sulfides, alkyl di-sulfides, alkali metal sulfonates and alkaline earth salts of sulfonic acids.

7. Miscellaneous ring compounds comprising mercapto benzothiazole, oxazines, phenthiazine, indane and acridane.

8. Organic phosphorus compounds comprising oil-soluble phosphines, esters of phosphorous acid and esters of phosphoric acid.

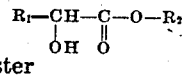
The invention in its more specific aspects involves the combination in hydrocarbon lubricating oils of metal phenates and an oxidation inhibitor for the oil effective at temperatures above 300° F. in the presence of the metal phenate. Not all of the above listed anti-oxidants satisfy this more rigid requirement and many of them are therefore not fully equivalent to the preferred species utilized in the present invention. Examples of types of high temperature oxidation inhibitors for hydrocarbon oils comprise metal salts of substituted acids of phosphorus, certain oil-soluble esters of carboxylic acids containing an active group, alkali metal sulfonates, alkaline earth metal sulfonates, alkaline earth organo-borates, alkaline earth organo-arsenates and naturally occurring inhibitors which may be extracted from mineral oil fractions. By the terms "alkaline earth organo-borates" and "alkaline earth organo-arsenates" it is intended to designate alkaline earth metal salts of acids of boron or acids of arsenic which contain an organic substituent. The organic substituent may be an alkyl, aryl, alkaryl, aralkyl or a cyclic non-benzenoid group. Alkyl substituents are at present preferred.

The following comprise examples of inhibitors of the ester type having the above mentioned active groups:

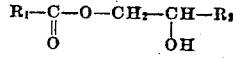
Di-ethyl tartrate, di-butyl tartrate, di-amyl tartrate, di-iso-amyl tartrate, di-benzyl tartrate, di-octyl tartrate, di-lauryl tartrate, amyl lactate, octyl lactate, tri-iso-amyl citrate, di-amyl mucate.

The active grouping in these compounds comprises a hydroxyl group in the alpha or beta position relative to the carboxyl group. These types of compounds may be represented generically by the following structural formulae:

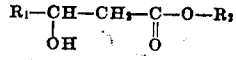
Alpha hydroxy ester



Beta hydroxy ester



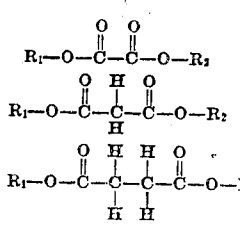
or



in which R_1 and R_2 represent an alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid group.

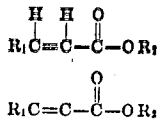
A second series of inhibitors of the ester type having an active group comprises oxalates, malonates and succinates of ethyl, propyl, butyl, amyl and the like alcohols. The neutral esters of these polycarboxylic acids are preferred.

The active grouping in the above second series of esters comprises two carboxyl groups no more than two carbon atoms apart and may be represented generically by the following structural formulae:



A third series of esters containing an active group comprises ethyl, propyl, butyl, amyl and octyl esters of maleic, fumaric, acrylic and crotonic acids. The active grouping in these compounds comprises an unsaturated carbon-to-carbon bond conjugated with the carboxyl group.

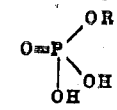
These types of compounds may be represented by the following structural formulae:



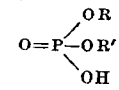
in which R_1 and R_2 may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid groups.

Metal salts of substituted acids of phosphorus illustrate another type of oxidation inhibitor which is effective at high temperatures in the combination of this invention. Metal salts of this type which may be utilized comprise salts of metals selected from Groups I, II, III, IV and VI of Mendeleeff's Periodic Table of the Elements. Specific examples of such metals are aluminum, calcium, barium, strontium, chromium and magnesium. Salts of iron, cobalt, nickel, zinc, sodium potassium and ammonium comprise additional examples of compounds falling within the broader aspects of the invention. The following comprise specific examples of metal salts of substituted acids of phosphorus, illustrating this type of oxidation inhibitor: aluminum lauryl phosphate, aluminum cetyl phosphate, aluminum octadecyl phosphate, aluminum "spermol" phosphate, aluminum oleyl phosphate, aluminum "spermenyl" phosphate, aluminum di-(cyclohexanyl) phosphate, aluminum (cetyl phenyl) phosphate, aluminum di-(amylphenyl) phosphate, aluminum di-stearo-glyceryl phosphate, aluminum (tetra-chloro-octadecyl) phosphate, aluminum di-(6-chloro, 2-phenyl phenyl) phosphate, aluminum di-(3-methyl, 4-chloro phenyl) phosphate, aluminum naphthenyl phosphate, calcium lauryl phosphate, calcium cetyl phosphate, calcium octadecyl phosphate, calcium "spermol" phosphate, calcium oleyl phosphate, calcium "spermenyl" phosphate, calcium di-(cyclohexanyl) phosphate, calcium (cetyl phenyl) phosphate, calcium di-(amylphenyl) phosphate, calcium di-stearo-glyceryl phosphate, calcium (tetra - chloro - octadecyl) phosphate, calcium di - (6-chloro, 2-phenyl phenyl) phosphate, calcium di-(3-methyl, 4-chloro phenyl) phosphate, calcium naphthenyl phosphate, chromium lauryl phosphate, chromium cetyl phosphate, chromium octadecyl phosphate, chromium "spermol" phosphate, chromium oleyl phosphate, chromium "spermenyl" phosphate, chromium di-(cyclohexanyl) phosphate, chromium cetyl phenyl phosphate, chromium di-(amylphenyl) phosphate, chromium di-stearo-glyceryl phosphate, chromium tetra-chloro-octadecyl phosphate, chromium di-(6-chloro, 2-phenyl phenyl) phosphate, chromium di-(3-methyl, 4-chloro phenyl) phosphate, chromium naphthenyl phosphate, barium lauryl phosphate, barium cetyl phosphate, barium octadecyl phosphate, barium "spermol" phosphate, barium oleyl phosphate, barium "spermenyl" phosphate, barium di-(cyclohexanyl) phosphate, barium cetyl phenyl phosphate, barium di-(amylphenyl) phosphate, barium di-stearo-glyceryl phosphate, barium tetra-chloro-octadecyl phosphate, barium di-(6-chloro, 2-phenyl phenyl) phosphate, barium di-(3-methyl, 4-chloro phenyl) phosphate, barium naphthenyl phosphate, as well as corresponding sodium, potassium, magnesium and ammonium salts.

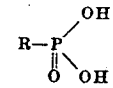
Metal salts of substituted acids of phosphorus illustrated by the above compounds comprise salts of substituted oxy-acids of pentavalent phosphorus of the following type formulae:



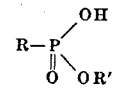
or



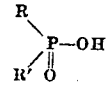
where R and R' may be alkyl, aryl, alkaryl, aralkyl, or cyclic non-benzenoid radicals. Substituted phosphoric acids containing at least twelve carbon atoms are preferred. Examples of preferred type acids are alkyl or alkaryl substituted phosphoric acids having at least twelve carbon atoms in the molecule. However, it is to be understood that the broader aspects of the invention include other types of substituted oxy-acids of phosphorus containing more than twelve carbon atoms. Additional examples of substituted oxy-acids of phosphorus which may be used in forming the metal salts of the present invention are as follows:



Phosphonic acid



Mono-ester of phosphonic acid



Phosphinic acid

In all of the above formulae R and R' may be alkyl, aryl, alkaryl, aralkyl, or cyclic non-benzenoid groups.

As has been previously pointed out, the present invention embraces the discovery that hydrocarbon oils containing both the metal salt of a phenol and an oxidation inhibitor have new and unpredictable advantages. The properties of hydrocarbon oils containing both a metal phenate and an anti-oxidant are illustrated by the following discussion and data.

A lubricating oil containing a metal phenate and a high temperature anti-oxidant effective above 300° F. in the presence of a phenate is more efficient in the lubrication of internal combustion engines than is an oil containing either of the components alone. In engine tests it has been found that metal phenates permit the formation of an orange-colored gum on the lower portion of the pistons of Diesel engines after prolonged periods of operation. A high temperature oxidation inhibitor comprising a metal salt of a substituted acid of phosphorus, such as calcium cetyl phosphate, permits slight thermal decomposition of the lubricating oil and some deposition of carbon in the top piston ring grooves of Diesel engines under severe conditions of operation. By using these two types of ingredients in combination in the lubricating oil, each of which has a disadvantage, a lubricating oil having neither of the above described objections is obtained and both formation of gum on the piston skirt and deposition of carbon in the piston ring grooves are prevented or inhibited.

It has also been observed that hydrocarbon oils

containing an inhibitor comprising a metal salt of a substituted phosphorus acid such as calcium cetyl phosphate forms a black deposit when contacted with metal surfaces heated to 425° F. or above. The presence of the phenate in an oil containing such metal phosphate salts prevents deposits up to temperatures above 550° F. This property of and cooperation between the two ingredients is illustrated by a test in which a heated metal surface (hot wire) is contacted with the compounded oil at 300° F. and the temperature gradually raised to 550° F., at which point it is maintained for one hour. In this test the hot wire is partially immersed and partially exposed in air and the amount of deposition at the oil surface is observed. The temperature at which initial decomposition of the oil takes place and the weight of the deposit on this wire after the test is completed are ascertained. The following data illustrate the improvements resulting in the above described test from the combination of ingredients disclosed herein:

Oil	Gum at oil surface	Decomposition temperature at oil surface	Wt. of gum deposited
Western oil, acid refined, S. A. E. 30	Heavy at 400° F.	None at 550° F.	.0005
Western oil, acid refined, S. A. E. 30+1% calcium cetyl phenate	Trace at 550° F.	None at 550° F.	.0000
Western oil, acid refined, S. A. E. 30+1% calcium cetyl phosphate	Light at 500° F.	425° F.	.0767
Western oil, acid refined, S. A. E. 30+½% calcium cetyl phenate+¼% calcium cetyl phosphate	Clean	None at 550° F.	.0000

An additional new result obtained by the combination of inhibitors utilizing this invention comprises increased stability of the oil solution of each of said components. Lubricating oils containing the metal phosphates alone may become cloudy in storage and the metal salts of substituted acids of phosphorus tend to precipitate from the oil solution in the presence of moisture. The presence of the phosphates alone in the oil also increases susceptibility to foaming. Metal phenates are susceptible to precipitation from solution in lubricating oils or cloud formation in the presence of water. When both the phenate and phosphate are present in the lubricating oil the solution is stable in the presence of water and precipitation or cloud formation does not occur in storage. Likewise, the foaming tendency of the oil is no longer apparent. Thus, the metal phenates act as a stabilizing agent for the metal salts of the substituted acids of phosphorus and permit the preparation of more concentrated solutions of the salts than might otherwise be obtained.

An additional indication of the properties possessed by mineral lubricating oils containing the combination of ingredients herein disclosed comprises an oil wetting test in which the ability of the oil to wet and adhere to hot metal surfaces is ascertained. In this test a trough is tilted at a 1° angle and heated at its lower end only so that a temperature gradient from the hotter lower end to the cooler upper end of the trough is obtained. The 1° angle at which the trough is tilted produces a force of 0.2 dynes, by reason of the action of gravity, upon oil placed in the trough. In this apparatus oil placed in the trough will flow uphill against gravity to the cooler metal surface until an equilibrium is reached between the force of gravity and the forces producing preferential wetting of the cooler metal surface. The hottest point to which the oil will flow is designated the limiting adhesive temperature and is a measure of the ability of the oil to lubricate and spread over hot surfaces such as the upper portions of the cylinder walls of internal combustion engines. Obviously, the higher the limiting adhesive temperature the greater the value of the lubricant under the adverse conditions typified. The following data show the novel coordination between the ingredients of applicants' composition:

Oil	Limiting adhesive temperature
	° F.
Western oil, acid refined, S. A. E. 30	165
Western oil, acid refined, S. A. E. 30+.5% calcium cetyl phenate	225
Western oil, acid refined, S. A. E. 30+1% calcium cetyl phenate	300
Western oil, acid refined, S. A. E. 30+.35% calcium cetyl phosphate	260
Western oil, acid refined, S. A. E. 30+.5% calcium cetyl phenate+.35% calcium cetyl phosphate	500

It has also been observed that the presence of metal salts of substituted acids of phosphorus not only increases the efficiency of the compounded oil in inhibiting piston ring sticking, but that these salts or other oxidation inhibitors decrease corrosion of copper-lead and cadmium-silver bearing metals by lubricating oils containing metal phenates. The phosphates also lower the viscosity increase, neutralization number and A. S. T. M. naphtha insolubles of the used oils. These improvements are illustrated by the following data:

Compounded mineral oil	Copper-lead wt. loss, mg.			Cadmium-silver wt. loss, mg.			Viscosity increase, °F.		Neut. No.	A. S. T. M. - naphtha insolubles mg./10 gm. oil
	24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.	100	210		
Mineral oil+1% calcium cetyl phenate	6.8	63.3	125.7	2.2	12.1	12.1	457	11.7	3.08	93
Mineral oil+1% calcium cetyl phenate+.1% calcium cetyl phosphate	1.5	31.5	79.2	0	4.4	4.7	323	8.6	1.37	8
Mineral oil+1% calcium cetyl phenate+.1% potassium cetyl phosphate		2.5	28.3	0	0	0.6	202	5.1	1.74	2
Mineral oil+1% calcium cetyl phenate +.1% ammonium cetyl phosphate	13.9	37.5	62.0	1.5	2.0	2.1	307	8.3	1.15	65
Mineral oil+1% calcium cetyl phenate+.1% amyl tartrate	6.7	9.1	10.7	0	0	1.0	291	7.8	1.16	47
Mineral oil+1% calcium cetyl phenate+.1% mono cetyl dicresyl phosphate	10.7	35.4	52.9	0.2	0	0	351	8.2	2.77	81
Mineral oil+½% potassium cetyl phosphate	1.8	2.0	3.1	0	0	0.4	731	15.1	0.55	50
Mineral oil+½% calcium cetyl phosphate	0.2	0.0	0.4	0	0	0.1	188	5.7	0.38	
Mineral oil+½% calcium cetyl phenate+¼% calcium dectyl dithio phosphate	9.4	43.2	55.6	1.3	1.4	1.3	392	12.0	1.95	134
Mineral oil+¼% calcium dicetyl dithio phosphate	1.7	3.0	3.7	+0.2	0	+0.4	223	7.2	0.82	28
Mineral oil+1% calcium cetyl phenate+½% mono cetyl dicresyl phosphate	11.6	15.0	15.8	0.4	0.4	0.4	272	10.1	2.49	51
Mineral oil+1% calcium cetyl phenate+½% tetraphenyl tin	8.6	21.3	28.3	0.5	0.5	0.5	341	12.2	2.02	38
Mineral oil+½% calcium cetyl phenate+¼% calcium cetyl phosphate	0.2	1.0	1.2	0	0.2	0.1	210	5.2	1.49	27

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 plus or minus 1° F. of the test temperature which was 300° F. 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 metal were placed in the oils; in most cases the copper-lead mixture 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 determined that the wear rate on aluminum is materially improved by the presence of oxidation inhibitors such as metal salts of substituted acids of phosphorus and tartrate esters in compounded lubricating oils containing metal phenates. Also the wear rate of oils containing metal salts of substituted acids of phosphorus is materially improved on steel surfaces by the presence of a metal phenate. Thus one addition agent gives higher wear on aluminum and the other higher wear on steel surfaces, whereas a combination of the two yields an oil having a low wear rate on both aluminum and steel.

From the above detailed descriptions it will be apparent that the combinations of ingredients herein disclosed give a new composition having new and highly useful properties. It is immaterial for the purpose of the present invention whether the components be separately new or old since it is the discovery of the combination of ingredients and the unexpected properties obtained thereby which comprise applicants' contribution to the art.

The compounded lubricants 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 metals, Babbitt bearings are little, if at all, affected by such corrosive action. Hence, compounded oils 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 exteremely advantageous in conjunction with the operation of internal combustion engines having bearings of Babbitt or other corrosive resistant bearing metals. The present invention in its broader aspects is therefore not limited to the particular combination of ingredients having all or the greatest number of advantages but embraces various of the less advantageous addition agents which will find utility in particular applications where all the possible improvements in the properties may not be required or where the standard of performance may not be so high.

A moderately acid refined Western naphthenic base lubricating oil is the preferred base oil stock for the compounded lubricants involved herein. The compounding ingredients appear to function more efficiently in such a base oil than in paraffinic oil stocks or highly refined Western oils. However, it is to be understood that the invention is not limited to any particular base stock since advantages herein disclosed may be obtained, at least to some degree, with various oil stocks, the selection of which will be determined by conditions and service which the compounded lubricant is to encounter.

The proportion of oxidation inhibitors which may be added to mineral lubricating oils, according to the principles of the present invention, may vary widely depending upon the uses involved and the properties desired. As little as 0.05% by weight of various of the oxidation inhibitors gives measurable improvements, particularly as respects the color stability of the compounded oil. From approximately 0.1% to 2% of the compound may be added to lubricants containing metal phenates where stability at high temperature comprises the principal property desired. Solutions containing more than 2% of the compounds in mineral oils may be utilized for various purposes, e. g., for preparing lubricating greases and concentrates capable of dilution with lubricating oils and the like. Likewise, the proportion of metal phenates present in compounded lubricants may vary widely depending on the uses involved and the properties desired. As little as 0.1% by weight of the phenate gives measurable improvement, although from approximately 0.25% to approximately 2% phenate 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 various of the phenates may be dissolved in mineral oil for the purpose of preparing a concentrate capable of dilution with lubricating oils and the like. Concentrates containing high percentages of the phenate and an oxidation inhibitor comprise a convenient method of handling the 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 present in 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 mineral hydrocarbon oils containing in addition to the metal phenate and the oxidation inhibitor, 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.

The combination in hydrocarbon lubricating oils of a metal phenate and aromatic compounds having two or more polar substituents is claimed in our copending application Serial No. 479,260, filed March 15, 1943. The combination in hydrocarbon lubricating oils of a metal phenate and sulfides, disulfides and polysulfides is claimed in our copending application Serial No. 481,004, filed March 29, 1943.

While the character of the invention has been described in detail and numerous examples of the composition given, this has been done by way of illustration only and with the intention that no limitation should be imposed on the invention thereby. It will be apparent to those skilled in the art that 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 of matter comprising a hy-

drocarbon lubricating oil, a metal phenate having an oil-solubilizing substituent in an aryl radical thereof, and a hydroxy ester having at least one hydroxyl group no more than two carbon atoms removed from a carboxyl group of said ester, said ester being present in an amount sufficient to stabilize the oil against oxidation, and said phenate being present in an amount sufficient to augment the action of the inhibitor.

2. A composition of matter comprising a hydrocarbon oil, an alkaline earth metal phenate having an oil-solubilizing substituent in an aryl radical thereof, and a hydroxy ester having at least one hydroxyl group no more than two carbon atoms removed from a carboxyl group of said ester, said ester being present in an amount sufficient to stabilize the oil against oxidation, and said phenate being present in an amount sufficient to augment the action of the inhibitor.

3. A composition of matter comprising a hydrocarbon oil, a calcium phenate having an oil-solubilizing substituent in an aryl radical thereof, and a hydroxy ester having at least one hydroxyl group no more than two carbon atoms removed from a carboxyl group of said ester, said ester being present in an amount sufficient to stabilize the oil against oxidation, and said phenate being present in an amount sufficient to augment the action of the inhibitor.

4. A composition as in claim 1, in which the hydroxy ester is a tartrate.

5. A composition as in claim 1, in which the hydroxy ester is di-amyl tartrate.

6. A composition as in claim 1, in which the hydroxy ester is a lactate.

7. A composition as in claim 1, in which the hydroxy ester is amyl lactate.

8. A composition as in claim 1, in which the hydroxy ester is tri-amyl-citrate.

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Certificate of Correction

Patent No. 2,344,988. March 28, 1944.

FRANK W. KAVANAGH ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 8, for that portion of the formula reading

"$R_1C{=}C$" read $R_1C{\equiv}C$

and that the said Letters Patent should be read with this correction 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.

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