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COMPOUNDED MINERAL OIL

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This invention relates to a new and useful composition of matter and involves a composition comprising a viscous hydrocarbon oil and polyvalent metal salt of certain substituted acids of phosphorus.

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 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 lbs. per sq. in. Addition agents which render hydrocarbon oils resistant to deterioration by heat at high temperature levels in the order of those above mentioned usually impart to the oil the ability to inhibit piston ring sticking in internal combustion engines and permit longer periods of operation of such engines without the necessity of major overhauls heretofore occasioned by stuck piston rings.

It should be noted that stabilizing agents which are effective at low temperatures to impart increased stability to hydrocarbon oils, or which are effective at temperatures even as high as 200 or 250° F., are often ineffective under the more severe operating conditions and higher temperature levels to which lubricating oils are subjected in Diesel engines. Thus the operativeness of a stabilizer at atmospheric temperatures, or even temperatures as high as 200 to 300° F., gives no adequate basis for predicting the action of the same stabilizing agent at materially higher temperatures and under more severe operating conditions. The disclosures in the prior art relative to such stabilizers therefore cannot serve as a guide for one seeking stabilizing agents or oxidation inhibitors effective at higher temperature levels. The phenomena involved are catalytic in nature, are highly empirical and require extensive experimentation to determine the action of a given type of addition agent.

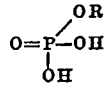
The present invention involves the discovery that dispersion of polyvalent metal salts of substituted oxy acids of phosphorus in hydrocarbon oils such as mineral lubricating oil imparts new, unpredictable and highly desirable properties to the composition. These new properties render the compounded oil particularly useful for various purposes. Although increased resistance to deterioration at high temperature levels comprises one of the principal advantages of the compounded oils of this invention, it is to be understood that the invention is not limited to this feature, that different compounds of the general type herein involved vary in their degree of effectiveness and may impart one or more other desirable properties to the lubricating composition. For example, certain of the compounds reduce the amount of wear produced as compared with a straight uncompounded mineral oil. The same or other compounds inhibit the corrosion of copper-lead or cadmium-silver bearing metals, etc. In general, however, it has been discovered that the new compositions herein disclosed are more stable to heat than is a hydrocarbon oil with which the compositions are compounded. The new compositions of this invention are therefore useful where resistance to deterioration by heat is important. An example of such utility, other than as a lubricating oil, comprises use as a heat transfer fluid where it may be desirable to inhibit or prevent the formation of a deposit on the metal surfaces from or to which heat is being conveyed. Likewise, the increased resistance to oxidation imparted to the oil by the compounds of this invention will find various applications as, for instance, in an insulating, switch, or transformer oil.

It has also been discovered that certain metal salts of substituted oxy-phosphoric acids have a combination of properties heretofore unknown and particularly desirable in compounded mineral oil, namely, the ability to inhibit oxidation and impart to lubricating oils increased resistance to deterioration by heat, the ability to inhibit piston ring sticking, freedom from the production of increased wear on cylinder walls and piston rings as compared with uncompounded mineral oils, and low corrosivity as respects the chemical action of the compounded oil on bearing metals such as cadmium-silver and copper-lead alloys. Although various compounded min-

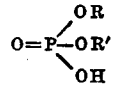
eral oils are known which are capable of inhibiting piston ring sticking, the discovery of specific compounding agents capable of imparting the above combination of properties to hydrocarbon oils represents an unobvious and important contribution.

Metal salts of substituted oxy acids of phosphorus which may be added to hydrocarbon lubricating oils to provide a new composition of matter of the type herein involved comprise the salts of metals selected from Groups II, III, IV and VI of Mendeléeff'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, tin and lead comprise additional examples of compounds falling within the broader aspects of the invention.

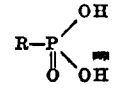
The metal salts of this invention are preferably formed from substituted oxy acids of pentavalent phosphorus of the following type formulae:



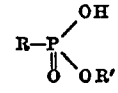
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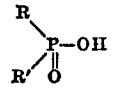
where R and R' may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. Substituted phosphoric acids containing at least twelve carbon atoms are preferred. Examples of preferred type acids are alkyl or alkaryl substituted phosphoric acids having at least twelve carbon atoms in the molecule. However, it is to be understood that the broader aspects of the invention include the use of 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.

In general, polyvalent metal salts of substituted derivatives of oxy acids of phosphorus such as phosphorous acid, hypophosphoric acid, H_2PO_3; orthophosphoric acid, H_3PO_4; pyrophosphoric acid, $H_4P_2O_7$; fall within the broadest aspects of the invention. By "substituted" or "substituted derivatives of" acids of phosphorus whenever used herein, it is intended to designate acids containing an organic group of the type previously listed, i. e., alkyl, aryl, alkaryl, aralkyl, or cyclic non-benzenoid groups. 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. The term "oxy acids of phosphorus" is intended to designate throughout the specification and claims acids of phosphorus in which one oxygen atom may intervene between the hydrogen and phosphorus atoms of the ester.

The preferred acids are substituted orthophosphoric acids and the preferred salts comprise the aluminum, calcium, barium and chromium salts of these acids. Examples of such salts are aluminum lauryl phosphate, aluminum cetyl phosphate, aluminum octadecyl phosphate, aluminum "spermol" phosphate, aluminum oleyl phosphate, aluminum "spermenyl" phosphate, aluminum cetyl phenyl phosphate, aluminum di-(amylphenyl) phosphate, aluminum naphthenyl phosphate, calcium lauryl phosphate, calcium cetyl phosphate, calcium octadecyl phosphate, calcium "spermol" phosphate, calcium oleyl phosphate, calcium "spermenyl" phosphate, calcium cetyl phenyl phosphate, calcium di-(amylphenyl) phosphate, calcium naphthenyl phosphate, chromium lauryl phosphate, chromium cetyl phosphate, chromium octadecyl phosphate, chromium "spermol" phosphate, chromium oleyl phosphate, chromium "spermenyl" phosphate, chromium cetyl phenyl phosphate, chromium di-(amylphenyl) phosphate, chromium naphthenyl phosphate, barium lauryl phosphate, barium cetyl phosphate, barium octadecyl phosphate, barium "spermol" phosphate, barium oleyl phosphate, barium "spermenyl" phosphate, barium cetyl phenyl phosphate, barium di-(amylphenyl) phosphate, and barium naphthenyl phosphate.

Additional examples of salts within the scope of the invention are: aluminum di-cyclohexanyl 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, calcium di-cyclohexanyl 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, chromium di-cyclohexanyl 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, magnesium dicyclohexanyl phosphate, magnesium di-stearo-glyceryl phosphate, magnesium tetra-chloro-octadecyl phosphate, magnesium di-(6-chloro, 2-phenyl phenyl) phosphate, magnesium di-(3-methyl, 4-chloro phenyl) phosphate, magnesium lauryl phosphate, magnesium cetyl phosphate, magnesium octadecyl phosphate, magnesium "spermol" phosphate, magnesium oleyl phosphate, magnesium "spermenyl" phosphate, magnesium cetyl phenyl phosphate, magnesium di-(amylphenyl) phosphate, magnesium naphthenyl phosphate, barium di-cyclohexanyl phosphate, barium di-stearo-glyceryl phosphate, barium tetra-chloro-octadecyl phosphate, barium di-(6-chloro, 2-phenyl phenyl) phosphate, and barium di-(3-methyl, 4-chloro phenyl) phosphate.

The substituted oxy acids of phosphorus utilized in the present inventiton 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 operation

is believed to be represented by the following equation:

$$ROH + C_2H_5OC_2H_5 + P_2O_5 \rightarrow RC_2H_4HPO_4 + C_2H_4PO_3$$

where R is an alkyl radical. The alkyl ethyl phosphoric acid is soluble in ether, while the ethyl meta phosphate is not and the ether solution of the former may be separated from the latter by decantation. Table 1 gives a number of examples of substituted phosphoric acids suitable for the purposes of this invention and a brief indication as to their method of preparation.

Table 1

Acid	Method of preparation
Mono-cetylphosphoric	9.25 lb. cetyl alcohol and 5.61 lb. P_2O_5 were refluxed with 5 gal. ethyl ether for 24 hr. Cetyl-phosphoric acid solution decanted.
Mono-"spermol" phosphoric	112 gms. solid sperm alcohols, 60 gms. P_2O_5, and 400 gms. ethyl ether treated as above.
Mono-octadecylphosphoric	100 gms. octadecanol and 150 c. c. benzene treated with 56.8 gms. $POCl_3$. Product was hydrolyzed to give a free acidic hydrogen.
Di-(6-chloro-2-phenyl-phenyl) phosphoric.	100 gms. of the phenol and 50 gms. P_2O_5 heated to 180° for 18 hours.
Mono-oleylphosphoric	107 gms. oleyl alcohol and 28.5 gms. P_2O_5 were refluxed in ethyl ether for 24 hours.
Mono-"spermenyl" phosphoric.	107 gms. liquid sperm alcohols and 27 gms. P_2O_5 refluxed in ethyl ether for 24 hours.
(Cetylphenyl) phosphoric	688 gms. cetyl phenol and 316 gm.s P_2O_5 refluxed with ethyl ether for 24 hours.
Di-(amylphenol) phosphoric	100 gms. amyl phenol and 43 gms. P_2O_5 heated to 185° F. for 15 hr.
Mono (tetrachloro) octadecyl-phosphoric.	190 gms. tetrachloro-octadecanol and 28 gms. P_2O_5 refluxed with ethyl ether for 17 hr.

In preparing the metal salts herein involved, the ethyl group in the ethyl phosphoric acid above mentioned may be hydrolyzed off to form the metal salt of the mono-alkyl-ortho-phosphoric acid, i. e. the salt of RH_2PO_4. This type of operation 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 the solution of the sodium or potassium salt by the addition of the appropriate metal ion. The salt may also be prepared by the direct neutralization of the acid as, for example, with lime where the calcium salt is to be obtained.

Basic aluminum salts prepared by the precipitation method are preferred by reason of their low corrosivity to alloy bearing metals although the so-called normal salts are not precluded. It is also preferred to maintain the amount of co-precipitated alkali metal salt in the heavy metal compounds at a minimum because the alkali metal salts decrease the stability of the oil solution in the presence of water.

The calcium salts may also be prepared in the non-aqueous environment by the reaction of calcium carbide with the free substituted acids of phosphorus.

The aluminum salts may also be prepared in an environment substantially free of water by the reaction of aluminum chloride with the free substituted acids of phosphorus. However, such aluminum salts have properties different from the salts prepared by precipitation from aqueous solutions. The salts prepared in a non-aqueous environment are soft, low melting solids, while the corresponding salts prepared by precipitation from aqueous solutions are hard, non-melting solids. Although the former type of salt may be utilized for imparting some desirable properties to hydrocarbon oils, it is preferred to use a salt prepared by precipitation from aqueous solutions where the ability to inhibit piston ring sticking in lubricating oils is desired.

By way of illustration and to demonstrate the unique properties possessed by the compounded oils of this invention, data from extensive tests are given in Table 2.

Table 2

Compound	Engine tests: Lauson: Percent of salt	Engine tests: Lauson: Ring sticking	Engine tests: Lauson: Cleanliness	Miscellaneous tests: Strip corrosion: Cu-Pb	Miscellaneous tests: Strip corrosion: Cd-Ag	Miscellaneous tests: Viscosity increase 100° F.	Miscellaneous tests: Weeks machine, wear, 300° F.	Preparation of compound: Acid	Preparation of compound: Salt prepared from—
	(1)			(2)			(3)		
Acid treated Western oil	0	1.0	Poor	1.0	1.0	477	1.0		
Aluminum lauryl phosphate	1.0	5.0	Good	0.1	1.5	546		Commercial lauryl phosphoric acid.	Na salt.
Do	0.05			0.1	0	195		do	Do.
Aluminum cetyl phosphate	1.6	5.0	Very good			450		Cetyl alcohol+P_2O_5+ether	Do.
Do	0.1	4.0	Good	0.2	0.7	161		do	Do.
Do	0.8	5±	do	0.6	0.7	146	0.58	do	K salt.
Aluminum octadecyl phosphate.	0.15	5.0	Very good	0.1	1.0			Octadecyl alcohol+$POCl_3$+C_6H_6.	Na salt.
Aluminum "spermol" phosphate.	1.0	5.0	do	Low	4.0			Solid sperm alcohols+P_2O_5+ether.	Do.
Do	0.7	5.0	do	1.0	1.0	211		do	Do.
Aluminum oleyl phosphate	0.7	4.0	Good	0.1	1.0			Oleyl alcohol+P_2O_5+ether	Do.
Aluminum "spermenyl" phosphate.	0.3	2.0	Fair	0.1	0.2			Liquid sperm alcohol+P_2O_5+ether.	Do.

(1) Expressed as ratio of time to stick rings of compounded oil to that with an uncompounded Western acid refined oil S. A. E. 30.
(2) Expressed as ratio of compounded oil corrosion to corrosion with Western acid refined oil S. A. E. 30.
(3) Expressed as ratio of wear of compounded oil to that of Western acid refined oil S. A. E. 30.
The base oil used for testing the addition agent was in all cases an acid refined Western oil S. A. E. 30 grade.

Table 2—continued

Compound	Engine tests: Lauson: Percent of salt	Engine tests: Lauson: Ring sticking	Engine tests: Lauson: Cleanliness	Miscellaneous tests: Strip corrosion: Cu-Pb	Miscellaneous tests: Strip corrosion: Cd-Ag	Miscellaneous tests: Strip corrosion: Viscosity increase 100° F.	Miscellaneous tests: Weeks machine, wear, 300° F.	Preparation of compound: Acid	Preparation of compound: Salt prepared from—
	(1)			(2)			(3)		
Aluminum di-cyclohexanyl phosphate.	0.1	5.0	Very good.					Cyclohexanol+P_2O_5+ether	Na salt.
Aluminum di-(amyl-phenyl) phosphate.	1.0	3.0	Fair	0.5	2.0	131		Amylphenol+P_2O_5	Do.
Aluminum di-stearo-glyceryl phosphate.	0.7	2.0	do					Glyceryl distearate+P_2O_5+ether.	Do.
Calcium lauryl phosphate	1.0	2.0	Fair	1.0	5.0	451		Commercial lauryl phosphoric acid.	Do.
Calcium cetyl phosphate	0.5	5±	Excellent			156		Cetyl alcohol+P_2O_5+ether	K salt.
Do	0.9	4±	Very good.	0.5	1.0	162	0.38	do	Do.
Chromium cetyl phosphate	0.8		do	0.3	0.2	220		do	Na salt.
Do	1.0	5.0	do			199		do	Do.
Magnesium lauryl phosphate	1.0	2.0	Fair	9.0	49.0	401		Commercial lauryl phosphoric acid.	Do.
Aluminum lauryl phosphite	0.3	1.0	do	0.1	0.5	284		Lauryl alcohol+PCl_3	Do.

(1) Expressed as ratio of time to stick rings of compounded oil to that with an uncompounded Western acid refined oil S. A. E. 30.
(2) Expressed as ratio of compounded oil corrosion to corrosion with Western acid refined oil S. A. E. 30.
(3) Expressed as ratio of wear of compounded oil to that of Western acid refined oil S. A. E. 30.
The base oil used for testing the addition agent was in all cases an acid refined Western oil S. A. E. 30 grade.

The above data show that small amounts of most of the addition agents act as corrosion inhibitors even in acid treated Western oils which are ordinarily considered non-corrosive. Likewise, extremely low wear rates were obtained with the two compounded oils tested in the Weeks machine. All of the addition agents improved piston cleanliness and imparted resistance to piston ring sticking in engine tests.

In the above piston ring sticking tests a single cylinder 2⅝ inch bore, 2½ inch stroke Lauson gasoline engine was operated under extremely severe conditions for the purpose of developing fully piston ring sticking and piston gumming tendencies under circumstances simulating severe operating conditions encountered in the field. Operation of the motor during tests was continuous at 1600 R. P. M. except for shutdowns at fifteen-hour intervals for inspection. The jacket temperature was maintained at 375° F. and the sump oil temperature at 220° F.

The wear tests were carried out in a Weeks machine comprising a ½ inch steel ball pressed against a 1⅜ inch steel cylinder with a force of 40 lbs., the cylinder dipping in the oil to be tested and rotating at 600 R. P. M. The duration of the test was sixteen hours and the wear rate determined by measuring the amount of metal removed from the ball. In the above wear tests the lubricant was maintained at approximately 300° F. as indicated.

The 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 ±1° F. of the test temperature which was 300° F. Approximately 300 c. c. of oil under the 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 cut to size and 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.

To further illustrate the corrosion inhibiting properties of the compounding agents herein disclosed, the following data obtained in the above type strip corrosion test are given:

Table 3

Bearing metal \ Oil	Solvent treated Pennsylvania aircraft oil	Solvent treated Pennsylvania aircraft oil+.25% calcium cetyl phosphate
Weight loss milligrams-copper-lead	76.4	7.3
Weight loss milligrams-cadmium-silver	61.3	0.0
Weight loss milligrams-lead	415.4	267.4
Used oil inspections:		
Increase in viscosity at 100° F.	458	133
Increase in viscosity at 210° F.	18.7	3.8
Neutralization No.	0.65	0.57

The compounding agents herein disclosed may have one or more advantages, depending upon the particular compound selected, the proportion 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 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. The present invention in its broader aspects is therefore not limited to the use of a particular compound 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 improvement in properties may not be required or where the standard of performance may not be so high.

Present experience indicates that where the properties desired involve the ability to stabilize

lubricating oils under severe operating conditions, such as those encountered in the lubrication of pistons and piston rings of internal combustion engines of the Diesel type, polyvalent metal salts of substituted oxy acids of pentavalent phosphorus containing more than twelve carbon atoms in the molecule and preferably containing an alkyl or alkaryl substituent should be utilized. It is to be understood that by "polyvalent metal salts" used in the above connection the alkaline earth metals are included.

A moderately acid refined Western naphthenic base oil is the preferred oil stock used as a base for the compounded lubricants involved herein. The compounding ingredients appear to function more efficiently in such a base oil than in a highly paraffinic oil stock or a highly refined Western oil. 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 metal salts of substituted oxy acids of phosphorus added to mineral lubricating oils may vary widely depending upon the uses involved and the properties desired. As little as 0.05% by weight of the compound gives measurable improvements, particularly as respects the color of the compounded oil after use in internal combustion engines. From approximately 0.25 to approximately 2% of the compound may be added to lubricants where ability to inhibit piston ring sticking comprises the principal property desired. Solutions containing more than 2% of the compounds in mineral oil may be utilized for the purpose of preparing lubricating greases and concentrates capable of dilution with lubricating oils and the like. Such higher concentrations comprise a convenient method of handling the compounds and may be used as addition agents for lubricants in general as well as for other purposes.

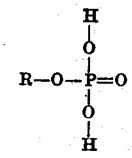
The metal salts of this invention may be added to hydrocarbon oils containing other compounding ingredients such as pour point depressors, oiliness agents, extreme pressure addition agents, blooming agents, compounds for enhancing the viscosity index of the hydrocarbon oil, corrosion inhibitors, color stabilizers, etc. The invention in its broader aspects embraces mineral hydrocarbon oils containing, in addition to metal salts of the substituted acids of phosphorus, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form greases, as in the case of mineral castor machine oils or other compounded liquid lubricants.

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:

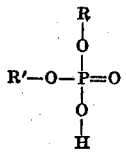
1. A composition of matter comprising a hydrocarbon oil and a magnesium salt of a substituted oxy acid of phosphorus.

2. A composition of matter comprising a viscous hydrocarbon oil and a magnesium salt of an acid of the type formula:



wherein R is a hydrocarbon radical.

3. A composition of matter comprising a viscous hydrocarbon oil and a magnesium salt of an acid of the type formula:



wherein R and R' are hydrocarbon radicals.

4. A composition of matter comprising a lubricating oil and a magnesium salt of a substituted oxy acid of pentavalent phosphorus containing an alkyl substituent and having more than twelve carbon atoms in the molecule.

5. A composition of matter comprising a hydrocarbon lubricating oil and a polyvalent metal salt of a substituted oxy acid of pentavalent phosphorus containing an alkaryl substituent and having more than twelve carbon atoms in the molecule.

6. A composition of matter comprising a hydrocarbon lubricating oil and a chromium salt of a substituted oxy acid of pentavalent phosphorus containing an alkaryl substituent and having more than twelve carbon atoms in the molecule.

7. A composition of matter comprising a hydrocarbon lubricating oil and a magnesium salt of a substituted oxy acid of pentavalent phosphorus containing an alkaryl substituent and having more than twelve carbon atoms in the molecule.

8. A composition of matter comprising a hydrocarbon lubricating oil and an aluminum salt of a substituted oxy acid of pentavalent phosphorus containing an alkaryl substituent and having more than twelve carbon atoms in the molecule.

9. A composition of matter comprising a hydrocarbon lubricating oil subject to deterioration at elevated temperatures, and from approximately 0.05% to approximately 2% by weight based on said oil of a metal salt of a substituted acid of phosphorus containing an organic substituent, the metal of said salt being selected from the class consisting of Groups II, III, IV and VI of Mendeléeff's Periodic Table of the Elements, said salt being of a type capable of inhibiting deterioration of said lubricating oil.

10. A composition of matter comprising a hydrocarbon lubricating oil subject to deterioration at elevated temperatures, and from approximately 0.05% to approximately 2% by weight based on said oil of a polyvalent metal salt of a substituted acid of phosphorus containing an organic substituent, said salt being of a type capable of inhibiting deterioration of said lubricating oil.

11. A composition of matter comprising a hydrocarbon lubricating oil and a minor proportion of a chromium salt of a substituted acid of phosphorus containing an organic substituent, said chromium salt being present in an amount sufficient substantially to inhibit deterioration of said oil.

12. A composition of matter comprising a hydrocarbon lubricating oil and a minor proportion of an aluminum salt of a substituted acid of phosphorus containing an organic substituent, said aluminum salt being present in an amount sufficient substantially to inhibit deterioration of said oil.

13. A composition of matter comprising a hydrocarbon oil and a polyvalent metal salt of an oxy-acid of pentavalent phosphorus containing an alkyl substituent and having more than twelve carbon atoms in the molecule.

14. A composition of matter comprising a hydrocarbon oil and a chromium salt of an oxy-acid of pentavalent phosphorus containing an alkyl substituent and having more than twelve carbon atoms in the molecule.

15. A composition of matter comprising a hydrocarbon oil and a chromium salt of a dibasic oxy-acid of pentavalent phosphorus containing a substituent of hydrocarbon structure.

16. A composition of matter comprising a hydrocarbon oil and a chromium salt of a dibasic alkyl substituted oxy-acid of pentavalent phosphorus.

17. A composition of matter comprising a hydrocarbon oil and a chromium salt of a dibasic cetyl substituted oxy-acid of pentavalent phosphorus.

18. A composition of matter comprising a hydrocarbon oil and a chromium salt of a monobasic oxy-acid of pentavalent phosphorus containing substituents of hydrocarbon structure.

19. A composition of matter comprising a hydrocarbon oil and a chromium salt of a monobasic oxy-acid of pentavalent phosphorus containing a substituent of hydrocarbon structure.

20. A composition of matter comprising a hydrocarbon oil and a chromium salt of a monobasic alkyl substituted oxy-acid of pentavalent phosphorus.

21. A composition of matter comprising a hydrocarbon oil and a chromium salt of a monobasic cetyl substituted oxy-acid of pentavalent phosphorus.

22. A composition of matter comprising a hydrocarbon oil and an aluminum salt of an oxy-acid of pentavalent phosphorus containing an alkyl substituent and having more than twelve carbon atoms in the molecule.

23. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a dibasic oxy-acid of pentavalent phosphorus containing a substituent of hydrocarbon structure.

24. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a dibasic alkyl substituted oxy-acid of pentavalent phosphorus.

25. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a dibasic cetyl substituted oxy-acid of pentavalent phosphorus.

26. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a monobasic oxy-acid of pentavalent phosphorus containing substituents of hydrocarbon structure.

27. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a monobasic oxy-acid of pentavalent phosphorus containing a substituent of hydrocarbon structure.

28. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a monobasic alkyl substituted oxy-acid of pentavalent phosphorus.

29. A composition of matter comprising a hydrocarbon oil and an aluminum salt of a monobasic cetyl substituted oxy-acid of pentavalent phosphorus.

30. A composition of matter comprising a hydrocarbon lubricating oil containing more than 0.05% by weight based on the oil of a polyvalent metal salt of a substituted acid of phosphorus containing an organic substituent.

31. An addition agent, capable of inhibiting piston ring sticking, for lubricating oils, comprising a concentrated solution in mineral oil of a polyvalent metal salt of a substituted acid of phosphorus containing an organic substituent, said solution being capable of dilution with mineral lubricating oil to form a homogeneous mixture containing from approximately 0.05% to 2% by weight of the polyvalent metal salt based on the total amount of lubricating oil.

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Certificate of Correction

Patent No. 2,228,659. January 14, 1941.

BRUCE B. FARRINGTON ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 3, after "and" insert the article *a*; page 3, first column, lines 14 to 43 inclusive, Table 1 should appear as shown below instead of as shown in the patent—

Table 1

Acid	Method of preparation
Mono-cetylphosphoric	9.25 lb. cetyl alcohol and 5.61 lb. P_2O_5 were refluxed with 5 gal. ethyl ether for 24 hr. Cetylphosphoric acid solution decanted.
Mono-"spermol" phosphoric	112 gms. solid sperm alcohols, 60 gms. P_2O_5 and 400 gms. ethyl ether treated as above.
Mono-octadecylphosphoric	100 gms. octadecanol and 150 c. c. benzene treated with 56.8 gms. $POCl_3$. Product was hydrolyzed to give a free acidic hydrogen.
Mono-oleylphosphoric	107 gms. oleyl alcohol and 28.5 gms. P_2O_5 were refluxed in ethyl ether for 24 hours.
Mono-"spermenyl" phosphoric.	107 gms. liquid sperm alcohols and 27 gms. P_2O_5 refluxed in ethyl ether for 24 hours.
Dicyclohexanylphosphoric	150 gms. cyclohexanol and 87 gms. P_2O_5 refluxed with 150 gms. ethyl ether for 24 hr.
(Cetylphenyl) phosphoric	688 gms. cetyl phenol and 316 gms. P_2O_5 refluxed with ethyl ether for 24 hours.
Di-(amylphenol) phosphoric	100 gms. amyl phenol and 43 gms. P_2O_5 heated to 185° F. for 15 hr.

page 3, first column, lines 51 to 61, Table 2, and page 4, first column, lines 2 to 12, Table 2—continued, the first two columns of the heading to the table should appear as shown below instead of as shown in the patent—

Compound	Engine tests		
	Lauson		
	Percent of salt	Ring sticking (1)	Cleanliness

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 March, A. D. 1941.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.