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COMPOUNDED MINERAL OIL

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12 Claims. (Cl. 252—35)

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

This application is a continuation-in-part of our parent application Serial No. 241,648, filed November 21, 1938, issued as Patent No. 2,228,659 on January 14, 1941, and is directed to a divisional aspect of the invention disclosed in the parent case.

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.

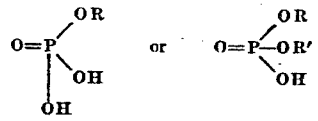
It should be noted that stabilizing agents which are effective at low temperatures to impart increased stability to hydrocarbon oils, or which are effective at temperatures even as high as 200 or 250° F., are often ineffective under the more severe operating conditions and higher temperature levels to 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 oxyacids 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.

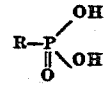
It has also been discovered that certain metal salts of substituted oxyphosphoric acids have a combination of properties heretofore unknown and particularly desirable in compounded mineral oil, namely, the ability to inhibit oxidation and impart to lubricating oils increased resistance to deterioration 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 mineral 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.

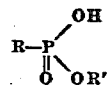
Metal salts of substituted oxyacids of phosphorus which may be added to hydrocarbon lubricating oils to provide a new composition of matter of the type herein involved comprise the salts of metals selected from groups II, III, IV and VI of Mendeleeff's Periodic Table of the Elements. Specific examples of such metals are aluminum, calcium, barium, strontium, chromium and magnesium. Salts of iron, cobalt, nickel, zinc, tin and lead comprise additional examples of compounds falling within the broader aspects of the invention.

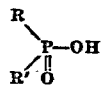
The metal salts of this invention are preferably formed from substitued oxyacids of pentavalent phosphorus of the following type formulae:



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 oxyacids of phosphorus containing more than twelve carbon atoms. Additional examples of substituted oxyacids of phosphorus which may be used in forming the metal salts of the present invention are as follows:

 phosphonic acid;

 monoester 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 oxyacids 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 "oxyacids 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 di-cyclohexanyl phosphate, magnesium di-stearo-glycerol 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 oxyacids 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 operation is believed to be represented by the following equation:

$$ROH+C_2H_5OC_2H_5+P_2O_5 \rightarrow RC_2H_5HPO_4+C_2H_5PO_3$$

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. 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 hrs. 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 cc. 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 hrs.
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 hrs.
Dicyclohexanyl phosphoric.	150 gms. cyclohexanol and 87 gms. P_2O_5 refluxed with 150 gms. ethyl ether for 24 hours.
(Cetylphenyl) phosphoric.	688 gms. cetyl phenol and 316 gms. P_2O_5 refluxed with ethyl ether for 24 hrs.
Di-(amylphenol) phosphoric.	100 gms. amyl phenol and 43 gms. P_2O_5 heated to 185° F. for 15 hrs.
Mono (tetrachloro) octadecylphosphoric.	190 gms. tetrachloro-octadecanol and 28 gms. P_2O_5 refluxed with ethyl ether for 17 hrs.

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. The 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 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 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.

The cobalt, nickel, zinc, tin and lead salts mentioned at page 4, line 19, and the oils containing the same may, by way of exemplification, be prepared as follows:

Cobalt cetyl phosphate: 100 gms. of cetyl phosphoric acid were suspended in 2½ gallons of water. This was neutralized with a 10% solution of potassium hydroxide, heated to 190° F. and the cobalt salt precipitated by adding an excess of a 10% cobalt chloride solution. 354 gms. of an acid refined naphthenic base S. A. E. 30 mineral lubricating oil were stirred in until it had picked up and dissolved the precipitated cobalt salt. The oil concentrate of the salt so produced was removed from the water by decanting and then washed several times by "working" with fresh water. The concentrate was dried by heating. The finished concentrate contained 25% by weight of cobalt cetyl phosphate. This concentrate was then added to an appropriate lubricating oil in the amount required to yield the proportions desired and hereinafter described.

Nickel cetyl phosphate was prepared by the method above described and using nickel chloride solution ($NiCl_2$) for precipitating the nickel cetyl phosphate from the potassium cetyl phosphate solution.

Zinc cetyl phosphate was prepared by the method above described and using zinc chloride solution ($ZnCl_2$) for precipitating the zinc cetyl phosphate from the potassium cetyl phosphate solution.

Tin cetyl phosphate was prepared by the method above described and using stannous chloride solution ($SnCl_2$) for precipitating the tin cetyl phosphate from the potassium cetyl phosphate solution.

Lead cetyl phosphate was prepared by the method above described and using the following proportions of ingredients:

Cetyl phosphoric acid	gms.	100
Water	gallons	2½
KOH solution	per cent	10
Lead acetate solution	do	10
Lubricating oil	gms.	164

The process yielded a concentrated solution containing 50% by weight of the lead cetyl phosphate.

Manganese cetyl phosphate was prepared by the method above described and using manganese sulfate solution ($MnSO_4$) for precipitating the manganese cetyl phosphate from the potassium cetyl phosphate solution.

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

Miscellaneous tests

Compound	Percent of salt	Engine tests, Lauson		Strip corrosion			Weeks machine wear 300° F.[3]	Preparation of compound	
		Ring sticking[1]	Cleanliness	Cu-Pb[2]	Cd-Ag[2]	Viscosity increase 100° F.		Acid	Salt prepared from—
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 octadecoyl phosphate	0.15	5.0	Very good	0.1	1.0			Octadecyl alchohl+$POCl_3$+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.
Aluminum di-cyclohexanyl phosphate.	0.1	5.0	Very good					Cyclohexanol+P_2O_5+ether	Do.
Aluminum di-(amyl-phenyl) phosphate.	1.0	3.0	Fair	0.5	2.0	131		Amylphenol+P_2O_5	
Aluminum di-stearo-glyceryl phosphate.	0.7	2.0	do					Glyceryl distearate+P_2O_5+ether.	Do.
Aluminum tetra-chloro-octadecyl phosphate.	0.1	3±	do	0.2	3.0	201		Tetra-chloro-octadecanol+P_2O_5+ether.	Do.
Calcium lauryl phosphate	1.0	2.0	do	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 shut-downs 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 pressure 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 cc. 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

In an identical strip corrosion test after 72 hours at 300° F. 1% cobalt cetyl phosphate decreased the loss in weight on a copper-lead bearing by 11.9 mm., lowered the viscosity increase

239 seconds Saybolt at 100° F., and lowered the naphtha insolubles (A. S. T. M.) formed by 360.

The limiting adhesion temperature is a significant property of lubricating oils, an increase in the limiting adhesion temperature being desirable. In a test designed to measure this property, 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 dyne 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 adhesion 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 adhesion temperature the greater the efficiency of the lubricant under the adverse conditions typified. The following data show the improvements produced, by way of example, with cobalt and lead salts:

TABLE 4

Oil	Limiting adhesion temperature—° F.
Acid refined naphthenic base S. A. E. 30	165
Ditto+1% cobalt cetyl phosphate	280
Ditto+1% lead cetyl phosphate	550+

In order to measure the ability of stabilizing agents to prevent or inhibit deterioration of the oil, color stability tests were carried out as follows: Weighed amounts of the oils under test were placed in 50 ml. beakers and set on a heated copper block having a uniform temperature distribution. The beakers were of uniform cross-section so that the level of the oil was the same distance from the bottom of the beaker in each case. The apparatus was protected from stray drafts so that still air was always in contact with the heated oil surface. The surface of the oil was not disturbed in any manner. It was necessary to acid-wash the beakers before each determination in order to destroy catalysts or inhibitors adsorbed on the surface of the glass. In the tests from which data are hereinafter given, the oil samples were heated at 360° F. for two hours.

A colorimeter was used for comparing the oxidized oil samples. This colorimeter contained two glass cells 50 mm. square by 7 mm. thick set equidistant from a light source consisting of a small electric light. The light from the source impinged on two photoelectric cells after passing through the oil samples contained in the glass cells. These two photoelectric cells were mounted in two arms of a Wheatstone bridge so that the differences in the two photoelectric currents could be determined. The oil before oxidation was placed in one glass cell and the darkened oil after oxidation was placed in the other. The difference in light transmission in the two oils was thus measured in a Wheatstone bridge, and the readings given in Table 5 are in terms of the scale on the Wheatstone bridge dial:

TABLE 5

Color stability

Oil	Color change
Paraffinic base S. A. E. 30:	47
Ditto+.5% nickel cetyl phosphate	26
Ditto+.5% zinc cetyl phosphate	21
Ditto+.5% tin cetyl phosphate	19
Ditto+.5% manganese cetyl phosphate	21
Acid refined naphthenic base S. A. E. 30:	21. 5
Ditto+.5% zinc cetyl phosphate	9
Ditto+.5% tin cetyl phosphate	15
Ditto+.5% manganese cetyl phosphate	11

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 oxyacids 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 oxyacids of phosphorus added to mineral lubricating oils may vary widely depending upon the uses involves 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 abiilty to inhibit piston ring sticking comprises the prin-

cipal 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.

In accordance with the foregoing disclosure, metal salts of metals of the iron family and acids of phosphorus containing an organic substituent may be utilized in lubricating oils in the proportions and for the purposes set forth hereinbefore. "Metals of the iron family" are known to be: chromium, manganese, iron, cobalt and nickel, and this term as used herein is intended to have this significance.

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 lubricating composition containing a salt of a metal of the iron family, said salt being of an acid of phosphorus having an organic substituent.

2. A lubricating composition containing a cobalt salt of an acid of phosphorus having an organic substituent.

3. A lubricating composition containing a nickel salt of an acid of phosphorus having an organic substituent.

4. A lubricating composition containing a manganese salt of an acid of phosphorus having an organic substituent.

5. A lubricant comprising a hydrocarbon oil and from approximately 0.05% to 2% by weight based on the oil of a salt of a metal of the iron family, said salt being of an acid of phosphorus containing an organic substituent.

6. A lubricant comprising a hydrocarbon oil and from approximately 0.05% to 2% by weight based on the oil of a cobalt salt of an acid of phosphorus having an organic substituent.

7. A lubricant comprising a hydrocarbon oil and from approximately 0.05% to 2% by weight based on the oil of a nickel salt of an acid of phosphorus having an organic substituent.

8. A lubricant comprising a hydrocarbon oil and from approximately 0.05% to 2% by weight based on the oil of a manganese salt of an acid of phosphorus having an organic substituent.

9. A liquid lubricating composition comprising a hydrocarbon oil subject to deterioration at elevated temperatures, and a small amount sufficient to inhibit said deterioration of a salt of a metal of the iron family, said salt being of an acid of phosphorus having an organic substituent.

10. A liquid lubricant composition comprising a hydrocarbon oil subject to deterioration at elevated temperatures, and a small amount sufficient to inhibit said deterioration of a cobalt salt of an acid of phosphorus having an organic substituent.

11. A liquid lubricating composition comprising a hydrocarbon oil subject to deterioration at elevated temperatures, and a small amount sufficient to inhibit said deterioration of a nickel salt of an acid of phosphorus having an organic substituent.

12. A liquid lubricating composition comprising a hydrocarbon oil subject to deterioration at elevated temperatures, and a small amount sufficient to inhibit said deterioration of a manganese salt of an acid of phosphorus having an organic substituent.

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