Patented Jan. 14, 1941 2,228,658

UNITED STATES PATENT OFFICE

2,228,658

COMPOUNDED MINERAL OIL

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No Drawing. Application November 21, 1938, Serial No. 241,647

27 Claims. (Cl. 252—39)

This invention relates to a new and useful composition of matter and involves a composition comprising a hydrocarbon oil and an alkaline earth 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, 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 alkaline earth 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. For example, oil soluble alkaline earth organo-phosphates like calcium cetyl phosphate, calcium lauryl phosphate, calcium cetyl phenyl phosphate, and calcium octadecyl phosphate are capable of imparting to crankcase lubricants in internal combustion engines increased color stability, resistance to sludging, and low wear rates while simultaneously inhibiting corrosion of modern bearing metals such as copper-lead and cadmium-silver alloys.

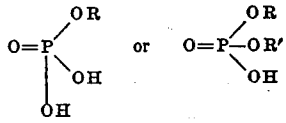
In general it has been discovered that the new mineral oil compositions herein disclosed are more stable to heat and more resistant to oxidation than is the hydrocarbon oil with which the compositions are compounded. The new compositions of this invention are therefore useful where resistance to deterioration by heat or oxidation is important. An example of such utility other than use as a lubricating oil comprises use as a heat transfer fluid where it may be desirable to inhibit or prevent the formation of deposits on the metal surface from or to which heat is being conveyed. 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 calcium salts of substituted phosphoric acids in particular have a combination of properties heretofore unknown and particularly desirable in compounded lubricating oils, namely: the ability to inhibit oxidation and impart to lubricating oils increased resistance to deterioration by heat; the ability to inhibit piston ring sticking; the ability

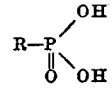
to decrease the wear rate on cylinder walls and piston rings as compared with uncompounded minerals oils; not only freedom from corrosive action on bearing metals such as cadmium-silver and copper-lead alloys, but the capacity to actually inhibit corrosion of such materials. Although various compounded 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 represent an unobvious and important contribution.

Alkaline earth metal salts of substituted oxy-acids of phosphorus which may be added to hydrocarbon oils to provide a new composition of matter of the type herein involved comprises salts of metals selected from Group II of Mendeleeff's Periodic Table of the Elements. Specific examples of such metals are calcium, strontium, and barium. The term "alkaline earth metals" as used herein is intended to designate generically the left hand sub-group of Group II of the Periodic Table.

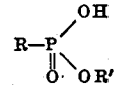
The metal salts of this invention are preferably formed from substituted oxy-acids of pentavalent phorus of the following type formulae:



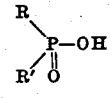
where R and R' may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. Preferably substituted phosphoric acids containing at least twelve carbon atoms are utilized. Examples of preferred type acids are alkyl or alkaryl substituted phosphoric acids having at least twelve carbon atoms in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

Alkaline earth metal salts of substituted derivatives of acids of phosphorus such as phosphorous acid, H_3PO_3; hypophosphoric acid, H_2PO_3; orthophosphoric acid, H_3PO_4; and pyrophosphoric acid, $H_4P_2O_7$, are regarded as falling 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 calcium salts of these acids. Examples of such salts are calcium lauryl phosphate, calcium cetyl phosphate, calcium octadecyl phosphate, calcium "spermol" phosphate, calcium oleyl phosphate, calcium "spermenyl" phosphate, calcium cetyl phenyl phosphate, and calcium di-(amylphenyl) phosphate. Additional examples of salts within the scope of the invention are: calcium di-stearo-glyceryl phosphate, calcium naphthenyl phosphate, calcium di-cresyl phosphate and calcium di-cyclohexanyl-phosphate.

The substituted oxy-acids of phosphorus utilized in the present invention may be prepared by methods known in the art. For example, a mixture of a higher alcohol and phosphorus pentoxide in ethyl ether may be refluxed for several hours. The reaction by which the substituted phosphoric acid is formed in this 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 meta phosphate is not and the ether solution of the former may be separated from the latter by decantation. Table I 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 I

Mono-cetylphosphoric	9.25 lb. cetyl alcohol and 5.61 lb. P_2O_5 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. ether treated as above.
Mono-octadecylphosphoric	100 gms. octadecyl alcohol and 150 c.c. benzene treated with 56.8 gms. $POCl_3$. Product was hydrolyzed.
Mono-oleylphosphoric	107 gms. oleyl alcohol (crude octadecenol) and 28.5 gms. P_2O_5 were refluxed in ethyl ether for 24 hr.
Mono-"spermenyl" phosphoric.	107 gms. liquid sperm alcohols and 27 gms. P_2O_5 refluxed in ethyl ether for 24 hr.
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 hr.
Di (amylphenyl) phosphoric	100 gms. amyl phenol and 43 gms. P_2O_5 heated to 185° F. for 15 hr.

In preparing the alkaline earth 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 alkaline earth 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 line where the calcium salt is to be obtained.

Where the metal salt is prepared by precipitation from a solution of the sodium or potassium salts of substituted orthophosphoric acids, it has been observed that the sodium or potassium salts are co-precipitated to some extent with the desired alkaline earth metal salt. It is preferred to maintain the amount of co-precipitated alkali metal salt in the alkaline earth metal compound at a minimum because the alkali metal salt decreases the stability of the oil solution in the presence of water.

The alkaline earth salts herein disclosed may be prepared in a non-aqueous environment by the reaction of the alkaline earth metal carbide, e. g., calcium carbide with the free substituted acids of phosphorus.

By way of illustration and to demonstrate the unique properties possessed by the compounded oils of this invention, the data in Table II are given:

Table II

Compound	Engine tests, Lauson			Miscellaneous data			
	Percent of salt	Ring sticking	Cleanliness	Strip corrosion Cu-Pb	Strip corrosion Cd-Ag	Vis. increase at 100° F.	Weeks machine, wear 300° F.
	(1)			(2)			(3)
None	0	1.0	Poor	1.0	1.0	477	1.0
Calcium lauryl phosphate	1.0	2.0	Fair	1.0			
Calcium cetyl phosphate	0.5	5.0±	Excellent			112	
Do	0.9	4.0±	Very good	0.5	1.0	145	0.38
Calcium (cetyl phenyl) phosphate	1.0	5.0		*1.0	*1.0	128	
Calcium cetyl phosphate	0.8	5.0		*2.0	*1.0	162	
Barium cetyl phosphate	1.0	5.0	Very good	1.0	1.0	127	0.3
Calcium (cetyl phenyl) phosphate	0.5			0.0	0.0	188	

(1) Expressed as ratio of time to stick rings of coumpounded 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.
*Indicates corrosion measured in Lauson engine during ring-sticking tests.

The above data show that compounds of the type herein disclosed impart to lubricating oils increased resistance to deterioration by heat or oxidation, inhibit piston ring sticking in internal combustion engines, increase the cleanliness of engine pistons, are essentially non-corrosive, actually inhibit corrosion of copper-lead and cadmium-silver bearings in strip corrosion tests, and reduce wear of metallic frictional surfaces. It has also been discovered that the alkaline earth metal salts of substituted oxy-acids of phosphorus form stable solutions in oil which are not easily precipitated. Tests show that the compounds herein disclosed are excellent oxidation inhibitors and color stabilizers for mineral hydrocarbon oils. Corresponding alkali metal salts are not equivalent to the alkaline earth salts by reason of the fact that the potassium salts, for example, 1% potassium cetyl phosphate in oil has caused scratching of the pistons, rings and cylinder liners of engines, and was easily precipitated from solution in the oil in the presence of water. The same is true of 1% sodium cetyl phosphate in oil.

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 periodic shutdowns at 15-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 at 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 16 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 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.

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, a compounded oil 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 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 improvements 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, alkaline earth 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 if the most efficient results are to be obtained.

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 alkaline earth metal salts of substituted oxy-acids of phosphorus added to mineral oils may vary widely, depending on 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 resistance to extremely high temperatures, such as encountered in Diesel engines, and ability to inhibit piston ring sticking comprise the principal properties desired. Solutions containing more than 2% of the compound 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 the concentrated solutions may be used as addition agents for lubricants in general, as well as for other purposes.

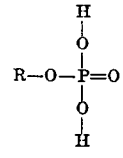
The metal salts of this invention may be added to hydrocarbon oils containing other compounding ingredients such as pour point depressors, oiliness agents, extreme pressure addition agents, blooming agents, compound for enhancing the viscosity index of the hydrocarbon oil, corrosion inhibitors, color stabilizers, etc. The invention in its broader aspects embraces mineral hydrocarbon oils containing, in addition to metal salts of 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:

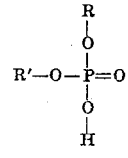
1. A composition of matter comprising a hydrocarbon oil and a strontium salt of a substituted oxy-acid of phosphorus containing an organic substituent.

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



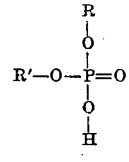
wherein R is a hydrocarbon radical.

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



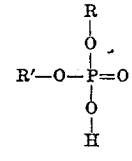
wherein R and R′ are hydrocarbon radicals.

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



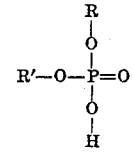
wherein R and R′ are hydrocarbon radicals.

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



wherein R and R′ are hydrocarbon radicals.

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



wherein R and R′ are hydrocarbon radicals.

7. A composition of matter comprising a lubricating oil and a strontium salt of an alkyl

substituted phosphoric acid containing more than twlelve carbon atoms.

8. A composition of matter comprising a lubricating oil and an alkaline earth metal salt of an alkaryl substituted phosphoric acid containing more than twelve carbon atoms.

9. A composition of matter comprising a lubricating oil and a calcium salt of an alkaryl substituted phosphoric acid containing more than twelve carbon atoms.

10. A composition of matter comprising a lubricating oil and a barium salt of an alkaryl substituted phosphoric acid containing more than twelve carbon atoms.

11. A composition of matter comprising a lubricating oil and a strontium salt of a alkaryl substituted phorphoric acid containing more than twelve carbon atoms.

12. A composition of matter comprising a hydrocarbon lubricating oil subject to deterioration at elevated temperatures, and a minor proportion based on said oil of an alkaline earth metal salt of a substituted acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to inhibit said deterioration.

13. 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 an alkaline earth 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.

14. A composition of matter comprising a hydrocarbon lubricating oil subject to deterioration at elevated temperatures, and a minor proportion based on said oil of a calcium salt of a substituted acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to inhibit said deterioration.

15. A composition of matter comprising a hydrocarbon lubricating oil subject to deterioration at elevated temperatures, and a minor proportion based on said oil of a barium salt of a substituted acid of phosphorus containing an organic substituent, said salt being present in an amount sufficient substantially to inhibit said deterioration.

16. 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 an alkaline earth metal salt of a substituted pentavalent oxy-acid of phosphorus containing an organic substituent, said salt being of a type capable of inhibiting deterioration of said lubricating oil.

17. 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 calcium salt of a substituted pentavalent oxy-acid of phosphorus containing an organic substituent, said salt being of a type capable of inhibiting deterioration of said lubricating oil.

18. A composition of matter comprising a hydrocarbon oil and an alkaline earth metal salt of an alkyl substituted acid of pentavalent phosphorus containing more than twelve carbon atoms in the molecule.

19. A composition of matter comprising a hydrocarbon oil and a calcium salt of an alkyl substituted acid of pentavalent phosphorus containing more than twelve carbons atoms in the molecule.

20. A composition of matter comprising a hydrocarbon oil and a barium salt of an alkyl substituted acid of pentavalent phosphorus containing more than twelve carbon atoms in the molecule.

21. A composition of matter comprising a hydrocarbon oil and an alkaline earth metal salt of a dibasic oxy-acid of pentavalent phosphorus containing a substituent of hydrocarbon structure.

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

23. A composition of matter comprising a hydrocarbon lubricating oil and from approximately 0.05% to approximately 2% by weight based on said oil of an alkaline earth metal salt of a substituted acid of pentavalent phosphorus containing an alkyl substituent of more than twelve carbon atoms.

24. A composition of matter comprising a hydrocarbon lubricating oil and from approximately 0.05% to approximately 2% by weight based on said oil of a calcium salt of a substituted acid of pentavalent phosphorus containing an alkyl substituent of more than twelve carbon atoms.

25. A composition of matter comprising a hydrocarbon lubricating oil and from approximately 0.05% to approximately 2% by weight based on said oil of calcium cetyl phosphate.

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

27. An addition agent, capable of inhibiting piston ring sticking, for lubricating oils, comprising a concentrated solution in mineral oil of an alkaline earth 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 alkaline earth metal salt based on the total amount of lubricating oil.

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