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MODIFIED LUBRICATING OIL

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This invention relates principally to lubricating oils, but may be extended also to other forms of lubricants such as greases, the so-called liquid greases and the like.

This application is a continuation in part of my prior application Serial Number 156,946, filed August 2, 1937.

The object of the invention is to produce lubricating oils and other lubricants having high film strength, good oiliness characteristics, resistance to oxidation and to corrosion as by inhibiting the development of oxidation and corrosive conditions in the lubricants.

I have discovered that by the addition of minor proportions of oil-soluble metal salts of alkyl esters of thio acids of phosphorus to lubricating oils, with or without the addition of other agents to the oils such as soaps and the like for the purpose of imparting detergent properties or thickening the oils, the resistance of oils to oxidation is greatly improved by what appears to be an inhibiting action on the part of the metal salts of the thiophosphates. Also the tendency to corrosion of metals by reason of the presence of some types of addition agents introduced into compounded oils to impart extreme pressure characteristics, is inhibited by these metallic derivatives of the phosphorus acids. This may apply to lubrication of gears, internal combustion engines, and other metal parts. Also the mentioned phosphates exert an inhibiting action against the development of conditions which are corrosive to highly corrosion-sensitive bearings in internal combustion engines and the like, such as Diesel engines and high-output aviation engines. For example, some highly refined lubricating oils have a tendency toward the development, apparently by oxidation, of acids corrosive to bearings such as cadmium-silver and copper-lead bearings while in use at the high temperatures found in internal combustion engines. Also similar corrosive acids tend to develop in some compounded oils while in use. Examples are oils which contain various detergent soaps now used in Diesel engines and the like. These soaps normally are added to the oils to overcome valve and ring sticking and the like and to keep the pistons and ring grooves clean. Such soaps include the oil-soluble metal soaps of various carboxylic acids such as chlorinated and phenylated fatty acids, oil-soluble metal soaps of high molecular weight acids derived from the oxidation of highly paraffinic petroleum fractions such as highly refined lubricating oils, and the like. These soaps, which may be alkaline earth metal

soaps or heavy metal soaps such as calcium, magnesium, barium, zinc, lead, manganese and aluminum soaps, tend sometimes, especially at the elevated temperatures of internal combustion engines, to catalyze oxidation with the formation of acids, possibly carboxylic acids, which are corrosive to the mentioned highly corrosion-sensitive copper-lead and cadmium-silver type.

I have found that by employing minor proportions of the metal thiophosphates of the present invention with these various oils or compounded oils, the tendency toward oxidation and the development of the corrosive conditions is materially inhibited. For example, I may employ in the order of from $\frac{1}{2}\%$ to 2.0% of various detergent soaps in an oil, and inhibit corrosion otherwise resulting from such soaps, by employing from 0.1% to 1.0% or 2.0% of one of the present metal thiophosphates as an inhibitor. These salts may also be added to compounded oils other than those mentioned. Again, I may add corresponding proportions of one of these metal thiophosphates to a highly refined highly paraffinic mineral lubricating oil and similarly inhibit oxidation and the development of corrosive conditions. This control of corrosion may or may not be the same type of control as that resulting where chlorinated or sulfurized extreme pressure agents are added to lubricants.

My invention therefore resides primarily in the employment in compounded or in uncompounded mineral lubricating oils, of minor proportions of oil-soluble metal salts of the thio acids of phosphorus substituted with organic radicals such as alkyl radicals which tend to render the salt oil-soluble. In addition to the mentioned alkyl groups, other alkyl organic substituents of sufficiently high molecular weight to render the salts oil-soluble may be employed, such as alkaryl radicals, alkylated cyclic radicals, and the like. Other suitable metals are the alkaline earth metals calcium, magnesium and barium, and the lighter of the so-called "heavy metals" such as zinc and aluminum, and other "heavy metals" such as lead, mercury, copper, manganese, iron, tin, bismuth, and thorium. For example, for the purpose of producing a most desirable extreme pressure agent I have employed zinc salts of octyl and di-octyl thiophosphates, and on an average about 1.0% thereof based on the oil in the case of lubricating oils, or total content if a grease, has been found very satisfactory. Other alkyls containing less than ten carbon atoms may be employed as substituents, so long as these render the salts oil-soluble. Examples

are the alcohols containing such groups as the various butyl, amyl, iso amyl, tertiary amyl, hexyl, heptyl, nonyl, and similar alkyl groups.

Salts of these produced from the various metals indicated are good inhibitors of oxidation and of corrosive conditions otherwise developed while in use, and are good inhibitors or retarders of corrosive conditions which result from the use of corrosive oiliness agents and the like containing halogens and corrosive sulfur, for example. The zinc salts have been found very desirable in the preparation of extreme pressure agents, and calcium and barium salts are very desirable as oxidation and corrosion retarders.

Instead of indicated alkyl groups as solubilizing constituents, alkylated phenyl, naphthalene and anthracene groups may be employed, including kindred alkylated aryl groups such as amyl-substituted phenol groups or octyl-substituted phenol or naphthyl or cresyl groups. Also alkylated cyclic groups may be employed such as obtained by the use of alkylated cyclic alcohols. All these alkyl groups, however, are to contain less than ten carbon atoms per group.

Thus, in all instances, the alkyl groups will contain preferably from 4 or 5 to 8 or 9 carbon atoms per group, whether these alkyls are attached to aryl groups or not.

A specific example of this invention which is particularly valuable as a high film strength and oiliness agent, and which also imparts some oxidation inhibiting value to oils compounded therewith, is zinc di-octyl thiophosphate. The corresponding lead salt is also useful. When zinc octyl thiophosphate (produced from zinc oxide and the reaction product of octyl alcohol and phosphorus pentasulfide as herein described) was used in an amount approximating 1.0% as an addition agent to lubricating oils, the load which the oil was capable of withstanding when tested by the well known Timken lubricant tester at 300 R. P. M. (described in S. A. E. Journal, vol. 28, 1931, pages 53-60) was increased from seven pounds without the agent to forty-five pounds when employing the agent. In addition to this film strength increase, the oil is made much more resistant to oxidation than in its original state. Moreover, the metallic salts of the alkyl thiophosphates in proportions here indicated inhibit, to a marked degree, the corrosion of metals by oils which contain sulfur, chlorine, corrosive sulfur compounds, corrosive halogenated bodies, or corrosive organic compounds containing sulfur or halogen. Where these corrosive materials are present in relatively large amounts somewhat more than 1.0% of alkyl thiophosphate may be used as necessary or desirable in accomplishing the desired end. In addition to the use of lead or zinc octyl thiophosphate, other indicated metal salts may be employed, and likewise other indicated alkyl thiophosphates of such metals may be used. Examples of such other metals are aluminum, calcium, magnesium and others herein indicated.

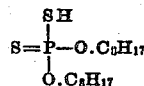
In referring to the content of 1.0% of the salt in the lubricating oil, it is not intended to convey the idea that this amount is critical. Varying proportions may be employed in mineral lubricating oils between any lower range sufficient to produce the desired increased film strength, or stabilization, or oxidation control, for example, 0.1%, up to a figure such as 20% beyond which added material produces no appreciable increased effect. For example, 10% of lead or zinc dioctyl thio-phosphate in an appropriate

mineral oil, produces a very valuable hypoid gear lubricant. For lubricating oils, smaller amounts within the solubility range of the particular salt will be used. Blends containing about one percent of the salt entirely inhibit the corrosion which normally takes place upon copper and steel when strips thereof are immersed in the lubricant for sixteen hours at 180° F. with water present and in contact with the strips.

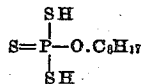
As an example of the preparation of the alkyl thiophosphates, octyl thiophosphate has been prepared readily by adding powdered phosphorus pentasulfide to octyl alcohol in a glass or ceramic container in the proportion of one gram mol to four gram mols, respectively, and agitating the mixture at temperatures of 250° F. to 300° F. until the phosphorus pentasulfide has been dissolved. This liquid product is then treated at similar temperatures with an excess of a powdered metal or metallic oxide to form the corresponding metal derivative. For example, in order to prepare the zinc octyl thiophosphate, the material resulting from the treatment of octyl alcohol with phosphorus pentasulfide is agitated with powdered zinc or zinc oxide until no more of the metallic compound is dissolved.

Similar preparations can be made with other metals, although in most cases it is preferable to use the metallic oxide. The metallic derivatives of octyl thiophosphate and similar thiophosphates are easily soluble in mineral oils of both western and eastern types (naphthenic and paraffinic) and the oil solutions are therefore readily prepared by mere introduction of the salt and subsequent mild agitation. The term "octyl thiophosphate" used in this disclosure may refer to either the di- or the mono-octyl thiophosphate, although it is the di-octyl thiophosphate which is the principal product of the above preparation. This is usually true of the other phosphates.

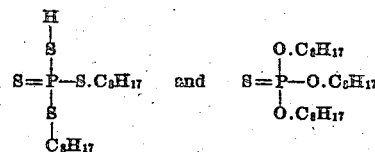
The specific material produced by the method above described showed rapid reaction with evolution of hydrogen sulfide when the temperature reached 250° F. The phosphorus pentasulfide had all gone into solution, that is had entered into chemical combination, in about two hours. This material analyzed 18.1% sulfur and 9.3% phosphorus. This indicated a product of the following composition:



There is some evidence of the presence of a mono-octyl thiophosphate which would have the formula:



Other possible combinations are:



The product produced as above described may be a mixture of all of these esters. The metal salts of these thiophosphates produced by the method above described were prepared by mixing the described ester with an excess of the oxides of the respective metals, such as zinc, lead, cop-

per, manganese, iron and tin, and allowing the resultant mixtures to stand overnight at about 250° F. Upon decanting and filtering, light colored viscous liquids were obtained except in the case of iron and manganese where the liquids were dark.

These various metal salts of the thiophosphate esters were blended in a highly solvent refined highly paraffinic western lubricating oil in the amount of about 1.0% of the ester to 99% of the oil, and tested on the well known Timken tester for extreme pressure characteristics. In each instance an increase in the film strength was noted as measured by the increase in load supported over that supported by the same oil untreated. Similar results were obtained by testing each of the materials in the same proportion in the same oil upon the S. A. E. extreme pressure lubricants tester.

Each of the above described blends was also subjected to a corrosion test and found to show definite inhibition of corrosion to metals, although some exhibited greater corrosion inhibiting properties than others. Similarly each blend was tested and found to possess distinct oxidation inhibiting properties in the oil at elevated temperatures.

The thio-salts previously described are adequately soluble in mineral lubricating oils, and are used according to this invention to control the sticking of piston rings and the like and also to stabilize the oil and to control other oxidation effects and tendencies to develop corrosive conditions in lubricating oils when used in internal combustion engines and the like, especially under the high temperature conditions of severe service engines such as Diesel engines. Calcium and zinc dioctyl phosphates are good examples. Around 0.5% to 1.0% probably will be commonly used for lubricating oils although proportions between about 0.3% and 2.0% will be in order and possibly for some uses as low as 0.1% or 0.2% and perhaps as high as 3% or 4%. This may depend on oil-solubility; lower molecular weight alkyl substituents imparting less solubility, but being more active and therefore requiring smaller proportions.

I claim:

1. A composition of matter comprising a hydrocarbon oil subject to deterioration at elevated temperature and a polyvalent metal salt of a sulfur containing substituted acid of phosphorus having an organic substituent therein, said salt being present in an amount sufficient substantially to inhibit said deterioration.

2. A composition as set forth in claim 1, in which the salt is a lead salt.

3. A composition as set forth in claim 1, in which the salt is a zinc salt.

4. A composition as set forth in claim 1, in which the salt is an aluminum salt.

5. A composition of matter comprising a hydrocarbon oil subject to deterioration at elevated temperatures and a polyvalent metal salt of a sulfur containing substituted acid of pentavalent phosphorus having an organic substituent therein, said salt being present in an amount sufficient substantially to inhibit said deterioration.

6. A composition as set forth in claim 5, in which the salt is a lead salt.

7. A composition as set forth in claim 5, in which the salt is a zinc salt.

8. A composition as set forth in claim 5, in which the salt is an aluminum salt.

9. A composition of matter comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a polyvalent metal salt of a thioester of phosphoric acid, said salt being present in an amount sufficient substantially to inhibit said deterioration.

10. A composition of matter comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a lead salt of a thioester of phosphoric acid, said salt being present in an amount sufficient substantially to inhibit said deterioration.

11. A composition as set forth in claim 9, in which the salt is a zinc salt.

12. A composition as set forth in claim 9, in which the salt is an aluminum salt.

13. A composition of matter comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a polyvalent metal salt of an ester of a thiophosphoric acid, said salt being present in an amount sufficient substantially to inhibit said deterioration.

14. A composition of matter comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a lead salt of an ester of a thiophosphoric acid, said salt being present in an amount sufficient substantially to inhibit said deterioration.

15. A composition as set forth in claim 13, in which the salt is a zinc salt.

16. A composition as set forth in claim 13, in which the salt is an aluminum salt.

17. A composition of matter comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a polyvalent metal salt of a thioacid of phosphorus, said salt being present in an amount sufficient substantially to inhibit said deterioration.

18. A composition as set forth in claim 17, in which the salt is a lead salt.

19. A composition as set forth in claim 17, in which the salt is a zinc salt.

20. A composition as set forth in claim 17, in which the salt is an aluminum salt.

21. A composition of matter comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a polyvalent metal salt of a thioester of a thiophosphoric acid, said salt being present in an amount sufficient substantially to inhibit said deterioration.

22. A composition comprising a hydrocarbon oil subject to deterioration at elevated temperature and an oil soluble polyvalent metal salt of an alkyl thiophosphate, said salt being present in an amount sufficient substantially to inhibit said deterioration.

23. A composition as set forth in claim 22, in which the salt is a lead salt in an amount of from approximately 0.1% to approximately 4% based on the weight of the oil.

24. A composition as set forth in claim 22, in which the salt is a zinc salt in an amount of from approximately 0.1% to approximately 4% based on the weight of the oil.

25. A composition as set forth in claim 22, in which the salt is an aluminum salt in an amount of from approximately 0.1% to approximately 4% based on the weight of the oil.

26. A composition comprising a hydrocarbon oil subject to deterioration at elevated temperature and an oil soluble metal salt of an alkyl thiophosphate in which the alkyl group contains less than ten carbon atoms, said salt being present in an amount sufficient substantially to inhibit said deterioration.

27. A composition as set forth in claim 26, in which the salt is a lead salt.

28. A composition as set forth in claim 26, in which the salt is a zinc salt.

29. A composition as set forth in claim 26, in which the salt is an aluminum salt.

30. A composition of matter comprising a hydrocarbon oil subject to deterioration at elevated temperature and an oil soluble metal salt of a sulfur containing substituted acid of phosphorus having at least one organic substituent of eight carbon atoms therein in an amount sufficient substantially to inhibit said deterioration.

31. A composition as set forth in claim 30, in which the salt is a lead salt.

32. A composition as set forth in claim 30, in which the salt is a zinc salt.

33. A composition as set forth in claim 30, in which the salt is an aluminum salt.

34. A composition comprising a hydrocarbon oil subject to deterioration at elevated temperatures and an oil-soluble polyvalent metal salt of an octyl thiophosphate, said salt being present in an amount sufficient substantially to inhibit said deterioration.

35. A composition as set forth in claim 34, in which the salt is a lead salt.

36. A composition as set forth in claim 34, in which the salt is a zinc salt.

37. A composition of matter comprising a hydrocarbon oil subject to deterioration at elevated temperature and an oil soluble polyvalent metal salt of a sulfur containing substituted acid of pentavalent phosphorus having two organic substituents therein in an amount sufficient substantially to inhibit said deterioration.

38. A composition as set forth in claim 37, in which the salt is a lead salt.

39. A composition as set forth in claim 37, in which the salt is a zinc salt.

40. A composition as set forth in claim 37, in which the salt is an aluminum salt.

41. A composition comprising a hydrocarbon oil subject to deterioration at elevated temperatures and an oil-soluble polyvalent metal salt of a di-octyl thiophosphate, said salt being present in an amount sufficient substantially to inhibit said deterioration.

42. A lubricating oil containing a constituent corrosive to metal of the class consisting of sulfur, chlorine, sulfurized bodies, halogenated compounds, and metal corrosive organic compounds containing sulfur and halogens, and an oil-soluble polyvalent metal salt of a sulfur containing substituted acid of phosphorus having an organic substituent therein, said salt being present in an amount sufficient to reduce oxidation and corrosion.

43. A composition of matter as set forth in claim 5, in which the sulfur containing acid of pentavalent phosphorus employed to produce the polyvalent metal salt is obtained by reacting phosphorus pentasulfide with an alcohol.

44. A composition as set forth in claim 5, in which the salt is a lead salt and the sulfur containing acid of pentavalent phosphorus employed to produce the polyvalent metal salt is obtained by reacting phosphorus pentasulfide with an alcohol.

45. A composition as set forth in claim 5, in which the salt is a zinc salt and the sulfur containing acid of pentavalent phosphorus employed to produce the polyvalent metal salt is obtained by reacting phosphorus pentasulfide with an alcohol.

46. A composition as set forth in claim 5, in which the salt is an aluminum salt and the sulfur containing acid of pentavalent phosphorus employed to produce the polyvalent metal salt is obtained by reacting phosphorus pentasulfide with an alcohol.

47. A composition of matter as set forth in claim 5, in which the sulfur containing acid of pentavalent phosphorus employed to produce the polyvalent metal salt is obtained by reacting phosphorus pentasulfide with an aliphatic alcohol.

48. A composition of matter as set forth in claim 5, in which the sulfur containing acid of pentavalent phosphorus employed to produce the polyvalent metal salt is obtained by reacting phosphorus pentasulfide with an octyl alcohol.

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