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ANTIOXIDANT FOR ESTER BASE FUNCTIONAL FLUIDS

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ABSTRACT OF THE DISCLOSURE

The oxidation resistance of synthetic ester based lubricants is enhanced by incorporating in the lubricant small amounts of a complex alkali metal organophosphorus compound prepared by esterifying a polyhydric alcohol free of beta hydrogen with a carboxylic acid or acid derivative and a phosphorus acid or acid derivative to form a complex organophosphorus ester, and thereafter contacting the ester with an alkali metal base.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to novel complex alkali metal organophosphorus compounds useful as oxidation inhibitors for synthetic ester base functional fluids, and to ester base fluids containing such inhibitors which are useful as hydraulic fluids, heat transfer fluids, and lubricants, especially at high temperatures.

Description of prior art

The continuing development and improvement of high performance aircraft jet engines has created a continual demand for improved lubricants which are efficient over a wide range of operating temperatures and which are resistant to oxidation and thermal degradation. Jet aircraft engines in particular are found to operate with greater efficiency at higher temperatures, and consequently emphasis for improved jet engine lubricants has been with respect to their high temperature properties.

The special requirements of jet engines has led to the development of synthetic ester lubricants, the most popular being polyesters formulated from hindered alcohols such as pentaerythritol, dipentaerythritol and mixtures thereof. These synthetic esters form the lubricant base stock to which various compounds are added to enhance and control such properties as viscosity, corrosivity, oxidation stability, flammability, extreme pressure properties, and load-bearing ability.

Oxidation stability of the synthetic esters is reflected in the change in viscosity and corrosivity of the material after exposure to air at elevated operating temperatures. Typically, uninhibited lubricant formulations show large increases in both viscosity and corrosivity as a result of oxidation.

Numerous oxidation and corrosion inhibitors have been found for use in ester base lubricating compositions. For example, antioxidants such as phenothiazine, phenyl - 1 - naphthylamine, diaromatic secondary amines, and mixtures of alkali metal salts of carboxylic acids with arylamines are well known in the art. The known stabilizers, however, have one or more deficiencies which limit their use and make them unsatisfactory for current needs. Typically, these inhibitors either do not provide adequate oxidation resistance for modern high performance, high temperature jet engines, or they adversely affect other critical properties such as load-bearing ability.

It is accordingly an object of the present invention to provide additives which impart superior oxidation resistance to synthetic ester base functional fluids. It is a further object of this invention to provide oxidation inhibitors for ester base lubricants which do not adversely affect the load-bearing properties of the lubricants. It is yet another object of this invention to provide superior lubricants for modern high performance, high temperature jet engines.

SUMMARY

Synthetic ester base lubricants and particularly the lubricants derived from pentaerythritol and polypentaerythritol are stabilized against oxidation at elevated temperatures by incorporating in the ester an inhibiting amount of a complex alklai metal organophosphorus compound prepared by esterifying a polyhydric alcohol free of beta hydrogen with an acylating agent which is a carboxylic acid or acid derivative and a polybasic acid of phosphorus or equivalent derivative thereof to produce a mixed acid ester of the polyol having both carboxylic acid and phosphorus acid residues, and contacting the acid ester with an alkali metal base to yield a complex alkali metal organophosphorus salt inhibitor.

The inhibitors can be prepared separately and added to the ester base stock lubricant, or where the lubricant base stock is an ester derived from a polyhydric alcohol free of beta hydrogen, the inhibitors can be prepared in situ by causing the phosphorus acid or acid derivative to react with the base stock itself to form the complex mixed organophosphorus ester, and then contacting the ester with an alkali metal base.

The incorporation of the complex alkali metal organophosphorus inhibitors of this invention into synthetic ester lubricant base stocks and hydraulic fluids substantially decreases the rate of oxidation of these fluids at elevated temperatures and does not adversely affect either the corrosivity or the load-bearing capability of the fluid.

DESCRIPTION OF PREFERRED EMBODIMENTS

In general, the alkali metal organophosphorus compounds employed as oxidation inhibitors in this invention are prepared by esterification of a polyhydric alcohol free of beta hydrogen, hereinafter referred to as a polyol, with a slight excess of a mixture of a carboxylic acid and a phosphorus acid or acid derivative, recovering the complex organophosphorus ester product, and contacting the ester with an alkali metal base to form a complex alkali metal organophosphorus compound.

Useful carboxylic acids are the mono- and polycarboxylic acids generally, and include those having straight, branched or cyclic hydrocarbon structures. The carboxylic acids may be saturated or unsaturated and the monocarboxylic acids may contain from about 4 to 22 carbon atoms while the polycarboxylic acids may contain up to 50 or more carbon atoms. The generally preferred acids are the monocarboxylic acids or mixtures of mono- and dicarboxylic acids wherein the monocarboxylic acid is represented by the structure RCOOH and R is an alkyl, aryl, alkaryl, or alicyclic hydrocarbon. Illustrative of useful monocarboxylic acids are the common aromatic acids such as benzoic, naphthoic or furoic acid, the alkyl aromatic acids such as alkyl-substituted benzoic and naphthoic acids wherein the alkyl is from 1 to about 8 carbon atoms, and alicyclic monocarboxylic acids such as cyclohexane monocarboxylic acids. The generally preferred monocarboxylic acids, however, are the acyclic acids having from about 4 to 12 carbon atoms and including specifically the fatty acids and the common branched chain acids such as isovaleric, 2-ethyl hexanoic, isodecanoic, and 2-propylheptanoic acid.

Other suitable carboxylic acids include those substituted with halogens and with groups containing, for example, sulfur, oxygen, nitrogen and halogen. The base carboxylic

acid may be aromatic or aliphatic and contain from about 2 to 36 carbon atoms.

It is permissible to substitute for the carboxylic acid a derivative thereof such as an acid halide, acid anhydride, or an acid ester which affords the same ester product upon reaction with the polyol as is obtained with the carboxylic acid. Suitable acid derivatives include, for example, carboxylic acid chlorides and the methyl and ethyl esters of carboxylic acid.

The size and structure of the organic groups in the carboxylic acids affects the solubility of the material, and the optimum size of this group is determined largely by the nature of the polyol to be esterified and the type of base stock to be inhibited. For example, in the esterification of dispentaerythritol with a mixture of phosphorus acid and monocarboxylic acids, the monocarboxylic acids can contain up to about 18 carbon atoms while in the esterification of tripentaerythritol it is generally advantageous to use lower molecular weight acids of 4 to 8 carbon atoms.

Illustrative of the polyols useful in the preparation of the inhibitors of this invention which are polyhydric alcohols free of beta hydrogen are neo-pentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, 2-butyl-2-ethyl-1,3-propane diol, and the like.

The phosphorus compounds useful in the esterification of the polyol include the free acids of phosphorus such as phosphorous, phosphoric and the lower alkyl phosphonic acids and derivatives of such acids which are capable of esterifying the polyol. Examples of such useful derivatives of these acids include the various acid anhydrides, phosphites, pohsphonates, halophosphates, halophosphites, halopohsphonates, phosphorous amides and phosphonous amides.

The useful phosphorus derivatives number in the hundreds and no attempt will be made to enumerate all these derivatives since the specific compounds which are capable of esterifying the polyol and are desirable from a practical standpoint will be either known by, or readily determined by, one skilled in the art. For purposes of illustration, however, the following compounds are mentioned as being readily available, capable of performing the desired esterification reaction, and generally suitable for use in the present invention: phosphites such as trimethyl phosphite, triethyl phosphite, triisopropyl phosphite, and triphenyl phosphite, phosphonates such as dimethyl methyl phosphonate and dibutyl butyl phosphonate; halophosphates such as phosphorus oxychloride; halophosphites such as phosphorus trichloride and phosphorus bromide; halophosphonates such as methyl phosphonyl dichloride and chloromethyl phosphonyl dichloride; phosphorous amides such as N,N',N''-hexamethylphosphorus triamide; and phosphonous amides such as N,N'-tetramethylbutylphosphonous diamides.

In general, the free acids of phosphorus provide good results and are the preferred reactants, while the acid derivatives are useful as permissible alternatives to the preferred embodiment of this invention. The selection of the acid or acid derivative used in the preparation of the inhibitor can, however, affect the effectiveness of the complex alkali metal organophosphorus inhibitor, particularly with respect to fluid properties such as lead corrosion and load-carrying capability. For example, phosphorous acid has been found to provide somewhat better results than phosphoric acid with respect to the load-bearing properties of the inhibited lubricant. Phosphorous acid is accordingly the preferred acid and the preferred phosphorus reactant for use in combination with the carboxylic acid in the esterification of the polyol.

Although the preferred method of the present invention involves esterification of the polyol with a mixture of carboxylic acid and a phosphorus acid or their appropriate acid derivatives, it is, of course, possible to carry out a partial esterification with either of the acids alone, then complete the esterification with the second acid in a separate step. Such obvious modifications of technique are considered to be self-evident and within the general scope of the present invention.

The products prepared in accordance with this invention are necessarily a mixture of several different ester compositions which cannot be described completely or accurately by chemical structure. Accordingly, the inhibitor compositions of this invention are best defined in terms of a process by which they are prepared. The following description is directed toward a preferred embodiment of the invention wherein the inhibitor is prepared separately for later addition to the base stock, and where the esterification is conducted with a mixture of a monocarboxylic acid and phosphorous acid.

The esterification reaction can be carried out using conventional esterification methods. Typically, the polyol, monocarboxylic acid, and phosphorous acid are charged together with an azeotroping agent such as toluene to a stirred reactor equipped with a reflux condenser and water separator. The reactor is heated until reflux begins, generally at about 110° to 140° C., and continued for about 2 hours during which time the temperature of the reaction increases to about 165° C. The reactor temperature is then further increased to about 170° C. for about 30 minutes to complete the reaction. The water, toluene, and excess acids remaining in the reaction product are removed at the end of the reaction period by gradually reducing the reactor pressure to about 10 mm. Hg while maintaining a temperature of 150–160° C.

The time and temperature of the esterification reaction depend to a large extent upon the reactants and azeotroping agent employed. The values given above represent the more common conditions experienced in preparing various inhibitor compositions using toluene as the azeotroping agent in accordance with the method of this invention, but the values are not intended as final limits on the operating conditions contemplated to be within the scope of the present invention. The use of benzene as the azeotroping agent for example, would obviously result in significantly lower initial reflux temperatures. Generally, however, a temperature of at least about 130 C. for the greater part of the reaction time is preferred in order to achieve a satisfactory reaction rate.

The product of the esterification reaction is contacted with an alkali metal base which can be a hydroxide or a salt of a weak acid, such as an acetate or carbonate. The alkali metal can be K, Na, Li, Cs, or Rb, although potassium is generally preferred. As an alternative to the alkali metals we have found that certain metals of the rare earth series can also be used. The preferred metals of this series are lanthanum, cerium, and praseodymium, and lanthanum oxide or lanthanum hydroxide is particularly preferred as the base compound. It is, accordingly, a permissible variation of this invention that the inhibitor can be a complex rare earth metal organophosphorus compound as well as an alkali metal compound. However, for the sake of clarity in the remainder of the description of this invention, the references to the metal component of the inhibitor are simply to alkali metal with the understanding that the rare earth metals can be substituted therefor.

The reaction with the alkali metal base is accomplished by contacting the organophosphorus ester with the base material under agitation at elevated temperatures of about 120–160° C. Separation of the complex alkali metal organophosphorus compound from excess alkali metal base and insoluble salts by centrifuging or filtration yields the complex inhibitor of this invention.

The complex alkali metal organophosphorus inhibitor compositions of this invention contain both alkali metal and phosphorus as essential elements. We have found that for optimum performance the ratio of alkali metal to phosphorous in the base stock as derived from the in-

hibitor should be at least about 0.8:1, and is preferably from about 1:1 to about 4:1. This ratio is important to the extent that it affects the solubility and effectiveness of the inhibitor. In particular, we have found that at ratios of alkali metal to phosphorus appreciably less than 0.8, the effectiveness of the inhibitor decreases even though solubility is high, while at ratios significantly higher than 4:1, solubility and effectiveness both diminish. The ratio of alkali metal to phosphorus is specified in terms of that derived from the inhibitor of this invention in realization that the presence of neutral phosphate esters such as tricresyl phosphate in the base stock would alter the actual ratio of these elements but not the effective ratio of the inhibitor composition.

An oxidation inhibiting amount of alkali metal organophosphorus inhibitor is provided in the lubricant base stock. The concentration of the inhibitor is most conveniently expressed in terms of the alkali metal equivalent of the titratable base as determined by titrating a sample of the inhibited base stock with 0.1 N HCl in an acetone-water solvent using bromphenol blue as an indicator.

While the actual amount of inhibitor required will vary according to the inherent stability of the base stock, and the particular composition of the inhibitor itself, an amount of inhibitors sufficient to provide at least about 0.01 milliequivalents (meq.) of titratable base per 20 grams of base stock is generally required to be effective, and from about 0.02 to about 0.05 meq. is generally preferred. Amounts of inhibitor in excess of the preferred range can be used, the maximum amount being limited only by the solubility of the composition in the base stock or by economic considerations but usually no substantial improvement in fluid properties is obtained by exceeding a concentration of about 0.10 meq. of alkali metal per 20 grams of base stock. The effect of the inhibitor is to significantly improve the oxidation and corrosion resistance of the fluid at elevated temperatures while the load-carrying properties remain substantially unaffected.

The lubricant base stocks of this invention include as a major component an ester of lubricating viscosity which may either be a simple ester or a complex polyester. Included are diesters or dibasic acids and alcohols, diesters of monobasic acids and glycols, and polyesters of monobasic or dibasic acid and polyhydric alcohols.

The preferred base stock esters for this invention are those polyesters derived from polyhydric alcohols free of beta hydrogen such as neo-pentyl glycol, 2-butyl-2-ethyl-1,3-propane diol, trimethylolethane, trimethyolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, and mixtures thereof. Suitable aliphatic carboxylic acids with which these polyols can be esterified include n- and iso-butyric acid and the n-, iso- and neo-acids of pentanoic, hexanoic, heptanoic, pelargonic, decanoic, lauric, myristic, palmitic, stearic, etc.

The pentaerythritol and dipentaerythritol derived base stocks are particularly preferred for economic reasons as well as their resistance to high temperature oxidation. Typical examples of pentaerythritol and dipentaerythritol base stocks are pentaerythrityl tetrabutyrate, pentaerythrityl tetravalerate, pentaerythrityl tetracaproate, pentaerythrityl dibutyrate dicaproate, pentaerythrityl butyrate caproate divalerate, pentaerythrityl butyrate trivalerate, pentaerythrityl butyrate tricaproate, pentaerythrityl tributyrate caproate. Suitable dipentaerythrityl esters include dipentaerythrityl hexavalerate, dipentaerythrityl hexacaproate, dipentaerythrityl hexaheptanoate, dipentaerythrityl hexacaprylate, dipentaerythrityl tributyrate tricaproate, dipentaerythrityl trivalerate trinonylate and dipentaerythrityl mixed hexaesters of C_{4-10} fatty acids.

Typical examples of triester base stocks are trimethylolpropane tri-n-pelargonate, trimethylolpropane tricaprate, trimethylolpropane tricaprylate and the trimethylolpropane triester of mixed octanoates.

The alkali metal organophosphorus inhibitors of this invention are particularly effective when used in combination with other antioxidants such as the arylamines and the combined effect of the two compounds provide a fluid of exceptional stability. It is accordingly desirable and considered to be within the scope of this invention to use the inhibitors of this invention in combination with other known additives for ester base synthetic functional fluids in order to achieve the best possible combination of properties. Such known additives include, in addition to the arylamine antioxidants, corrosion inhibitors, V.I. improvers, E.P. agents, foam inhibitors, antiwear agents, dyes, and the like.

Arylamines useful in combination with the inhibitors of this invention include for example the diphenyl amines such as diphenyl amine, p-octyldiphenyl amine, p,p'-dioctyldiphenyl amine, and the like; N-phenylnaphthylamines such as N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine, N-(p-dodecylphenyl) - 2 - naphthylamine, and the like; dinaphthylamines such as di-1-naphthylamine, di-2-naphthylamine, and the like; phenothiazines including N-alkyl phenothiazine; and N,N'-diphenyl phenylenediamine and dipyridylamines.

Corrosion inhibitors such as aminoindazole, tolyltriazole, benzoquanamine, dihydroxy anthraquinone, di-t-butyl phenol, disalicylol propylene diamine, and the like, V.I. improvers such as the polymethacrylates, antiform agents such as the silicone oils, E.P. agents such as phosphorodithioates, and various dyes are all well known additives of the prior art which can be incorporated in combination with the complex organophosphorus salt inhibitor of this invention in order to enhance or control a particular property of the formulated fluid as desired.

The description heretofore has been primarily concerned with the preparation of the inhibitor for addition to the base stock material; however, the alkali metal roganophosphorus inhibitors of this invention can, as stated eariler, also be prepared in situ in base stock esters derived from polyols by deacylation of the fully carboxylated polyol with a phosphorous acid or acid derivative, followed by basification of the organophosphorus ester with an alkali metal base to form the complex metal compound. Thus, for example, when an ester base stock derived from dipentaerythritol is heated with phosphorous acid under reduced pressure, carboxylic acid is removed and a mixed polyol carboxylate phosphorous ester is formed. This ester can subsequently be reacted with an alkali metal base and the compounds derived are effective inhibitors which are amply soluble in the base ester and have minimal storage and compatibility problems.

The following examples are provided to illustrate the methods whereby the inhibitors of the present invention are formed, and to illustrate the improved properties of the ester base lubricants containing such inhibitors. All parts and percentages in the examples are by weight unless otherwise specified.

The test procedure used in the examples to evaluate the effectiveness of the inhibitor compositions were as follows:

Oxidation and Corrosion—Federal Test Method Standard 791—Method 5308.4, with the following modifications:

Temperature—450° F.
Time—72 hours.
Air—10 liters (dry).
Metals—Mg, Al, Cu, Fe, Ti, Ag.
Metal coupons—attached to a rod instead of being tied into cube shape.
Corrosion data—results reported for Mg and Cu only, the other metals being substantially unaffected by the fluids evaluated.

Lead Corrosion Test—Federal Test Method Standard 791—Method 5321, with the following modifications:

Temperature—375° F.
Time—5 hours.

Viscosity—ASTM D–445–61.

Ryder Load Test—ASTM D–1947–62T.

The modifications to the standard O & C Test and Lead Corrosion Test conditions were designed to increase the severity of the test and yield more meaningful results in anticipation of actual service conditions in high temperature, high performance jet engines.

EXAMPLE I

Preparation of inhibitor composition

To a 5-liter reactor equipped with a stirrer, reflux condenser and water separator were charged 3 moles of dipentaerythritol, 3 moles of crystalline phosphorous acid, 15.3 moles octanoic acid, and 200 ml. toluene. The reactants were brought to vigorous reflux at an initial temperature of 120–130° C. and water released during the esterification reaction was separated as formed. Reactor temperature was gradually increased over a 2-hour period to 160° C., and finally increased to 170° C. and held for 30 minutes to complete the reaction.

When the esterification reaction was complete as indicated by the lack of water of reaction, the reactor pressure was decreased to 10 mm. to remove water, toluene and other volatile materials. A light yellow complex organophosphorous acid ester was decanted from heavier insoluble materials such as polyphosphorous acids.

The complex acid ester was treated at 140° C. with 1.9 moles of anhydrous potassium carbonate (2 equivalents per equivalent of acid) added in small increments with vigorous agitation. After addition and reaction was complete, the potassium organo-phosphorus compound was separated from excess carbonate as a clear yellow filtrate. The atomic ratio of potassium to phosphorus in the inhibitor product was determined to be about 1.3.

EXAMPLE II

The complex organophosphorous compound prepared in Example I was added to a synthetic ester base stock comprised of a mixture of PE and diPE esters of C_5 to C_9 aliphatic acids containing approximately 2 percent arylamine antioxidant, 0.1 percent of a corrosion inhibitor, and 15 p.p.m. silicon oil defoamer.

The inhibitor was added to the base stock at four levels of concentration, and the inhibited fluid evaluated for oxidation and corrosion stability. The results obtained for fluids containing the inhibitor of this invention are compared in Table I below with the results obtained for the same base stock without the inhibitor, and for the same base stock inhibited with potassium octanoate (KC_8) and potassium neodecanoate (KC_{10}) as taught by the prior art.

TABLE I

Run	Inhibitor, meq. alkali metal/20 g. base stock	Lead corrosion, mg./in.²	Appearance	O & C Test: Percent viscosity increase	O & C Test: Mg loss	O & C Test: Cu loss	Ryder Test [1]
1	Control	0	Clear	(2)	−7.8	−0.5	100
2	0.02 KC_8	−57.2	Suspension	71	−0.43	−0.16	96
3	0.02 KC_{10}	−74.4	Clear	162	−3.7	−0.23	87
4	0.005	−1.8	do	(2)	−10.4	−0.54	
5	0.01	−1.0	do	173	−4.3	−0.30	
6	0.02	−3.2	do	54	−0.08	−0.21	104
7	0.045	−4.8	do	58	−0.04	−0.26	

[1] Test results reported as percent of control.
[2] Too viscous to measure.

Comparison of Run 5, a preferred embodiment of this invention, with the control (Run 1) and the prior art (Runs 2 and 3) clearly shows the generally superior results obtained with the inhibitor of this invention. Particular improvement over the control is noted in percent viscosity increase and Mg corrosion, while improvement over the prior art is noted in Pb corrosion, appearance, and Ryder Test.

EXAMPLE III

Three inhibitor compositions were prepared according to the general procedure of Example I by substituting butanoic, dodecanoic, octadecanoic, and 2-ethyl hexanoic acids for the octanoic acid. The effectiveness of the different inhibitor compositions at a concentration of 0.02 meq. K per 20 g. of the dipentaerythritol ester base stock of Example II was determined with the results shown in Table II.

TABLE II

Run	Inhibitor: Polyol	Inhibitor: Acid	Lead corrosion, mg./in.²	Appearance	O & C Test: Percent viscosity increase	O & C Test: Mg loss	O & C Test: Cu loss
8	DiPE	n-C_4	+16.5	Cloudy	79	0	−0.26
9	DiPE	n-C_8	−3.2	Clear	54	−0.08	−0.21
10	DiPE	n-C_{12}	−25.1	do	63	−0.16	−0.10
11	DiPE	C_5–C_{18}	−10.8	do	80	−0.42	−0.24
12	DiPE	(1)	−9.0	do	53	+0.01	−0.17

[1] Acid, 2-ethyl hexanoic.

NOTE.—Abbreviations for polyols and acids used in this and subsequent examples are as follows.
Polyol: PE=pentaerythritol; DiPE=dipentaerythritol; TriPE=tripentaerythritol; TMP=trimethylol propane.
Acid: n-C_4=butanoic acid; n-C_5=pentanoic acid; n-C_8=octanoic acid; n-C_{12}=dodecanoic acid; n-C_{18}=octadecanoic acid.

EXAMPLE IV

The general procedure of Example I was followed to prepare complex organophosphorous potassium compounds from other polyols and fatty acids. The inhibitors were evaluated in the ester base stock lubricant of Example II according to the procedure of Example II. Identification of the inhibitor compositions and the evaluation of the stabilized products are given in Table III.

TABLE III

Run	Inhibitor Polyol	Inhibitor Acid	Lead corrosion, mg./in.²	Appearance	O & C Test Percent viscosity increase	O & C Test Mg loss	O & C Test Cu loss
13	TMP	n-C8	+0.4	Cloudy	90	−0.16	0.27
14	PE	n-C4	+0.9	do	67	−0.89	−0.10
15	PE	n-C8	−0.2	do	208	−10.3	−0.34
16	TriPE	n-C8	−2.0	Clear	98	−0.06	−0.30

EXAMPLE V

A complex organophosphorous potassium inhibitor was prepared according to the procedure of Example I except the acid charge consisted of 6 moles of crystalline phosphorous acid and 12 moles of octanoic acid. The molar ratio of phosphorous acid to monocarboxylic acid was thereby increased to 1:2 as compared to the 1:5 ratio of Example I. In the table below, the data illustrate that the additive of this example was also effective in stabilizing the fluid against viscosity increase.

TABLE IV

Run	Inhibitor	Lead corrosion mg./in.²	Appearance	O & C Test Percent viscosity increase	O & C Test Mg loss	O & C Test Cu loss
17	Example I	−3.2	Clear	54	−0.08	−0.21
18	Example V		do	69	−3.3	−0.39

EXAMPLE VI

The fluid of Example I, Run 5, was evaluated by the Bearing Rig Test according to Federal Test Method Standard 791A, Method 3410, Type II conditions, at a bulk oil temperature of 440° F. and a bearing temperature of 500° F. The performance of the test fluid was compared with the same fluid minus the organophosphorus additive (Example I—Run 1), and with two commercial jet engine lubricating oils which were comparable pentaerythritol ester base fluids. The excellent performance of the test fluid as shown by the low deposit rating and viscosity increase figures is evidenced by the data in Table V.

TABLE V.—BEARING RIG PERFORMANCE

Run	Fluid	Deposit rating	Percent viscosity increase	Consumption rate, cc./hr.
19	Example I, Run 5, test	21	50	16
20	Example I, Run 1 control	48	406	
21	Commercial Fluid A	55	144	30
22	Commercial Fluid B	55	467	38

The preceding examples illustrate preferred embodiments of the present invention and many variations and procedures will be readily apparent to those skilled in the art. For example, as mentioned earlier, phosphorus acid derivatives can be substituted for the free acids in the esterification of the polyol, and the esterification with the phosphorus acid derivative and the carboxylic acid can be conducted as two separate steps.

The esterification of polyols with phosphorus acid derivatives is well known in the art. An article by Wadsworth et al. in the Journal of the American Chemical Society, 84, 610 (1962) describes the preparation of bicyclic phosphites by treating trimethylolethane with phosphorus trichloride under conditions of high dilution and using pyridine as an acid binding agent. In a similar manner, one can prepare the analogous cyclic phosphonates. The phosphorus esters thus prepared can be reacted with carboxylic acid to form an organophosphorus ester composition which in turn is reacted with the alkali metal base to yield the inhibitor composition of this invention.

Other references discuss the preparation of complex organophosphorus esters such as pentaerythritol phosphites by reacting pentaerythritol with phosphorus acid derivatives of the formula $(RO)_3P$ where R is an alkyl or aryl hydrocarbon of 1 to 20 carbon atoms, as for example triphenyl phosphite or tributyl phosphite.

Also described in the literature is the preparation of bicyclic phosphites, bicyclic phosphates, bicyclic thiophosphates, and bicyclic selenophosphates by transesterification of a triaryl phosphite or a trihaloaryl phosphite with pentaerythritol. The bicyclic organic derivatives of phosphorus thus attained can be reacted with a carboxylic acid to form a complex organophosphorus esterification product, and this product can in turn be reacted with an alkali metal base to yield the inhibitor composition of this invention.

The use of phosphorus acid derivatives in the preparation of the inhibitors of this invention, is further illustrated by the procedures given in Examples VII through IX as follows:

EXAMPLE VII

N,N',N''-hexamethyl phosphorous triamide

To a 5-liter pot equipped with a stirrer, fractionating column and still head, charge 3 moles of dipentaerythritol and 3 moles of N,N',N''-hexamethyl phosphorous triamide and about 400 ml. of toluene. Warm the mixture slowly until vigorous reflux ensues, and continue to reflux until dimethylamine ceases to be evolved. When the evolution of dimethylamine ceases, distill approximately 200 ml. of toluene from the system and charge about 17 moles of octanoic acid. The reaction is continued with the evolution of water to form a complex organophosphorus acid ester which is recovered and treated with potassium carbonate according to the method of Example I.

EXAMPLE VIII

Phosphorus trichloride

To a 5-liter pot equipped with a stirrer and reflux condenser, charge 3 moles of dipentaerythritol and 3 moles of cold (0–5° C.) phosphorus trichloride. Stir the slurry for about 8 hours while blowing a slow stream of nitrogen through the reactants to sweep out HCl. When this reaction is substantially completed, warm the mixture to about 70° and charge 200 ml. of toluene and 15.3 moles of octanoic acid to the reactor. The reaction is continued with the evolution of water to form a complex organophosphorus acid ester compound which is recovered and reacted with an alkali metal base according to the method of Example I.

EXAMPLE IX

Trimethyl phosphite

To a 5-liter pot equipped with stirrer, fractionating column and still head, charge 3 moles of dipentaerythritol and 3 moles of trimethyl phosphite. Add a few drops of triethylamine catalyst to the mixture and slowly warm until refluxing begins. Fractionate out approximately 8 moles of methanol from the system until methanol ceases

to be evolved. Add 15.3 moles of octanoic acid and 200 ml. of toluene and continue the reaction as described above in Example VIII to obtain an organophosphorus acid ester composition.

This procedure is equally applicable for use with other lower trialkyl phosphites in addition to trimethyl phosphite, and also for use with triphenyl phosphite.

The preceding examples are intended to illustrate variations in the procedures and methods which may be followed in preparing the inhibitor compositions of this invention. Other modifications within the invention are possible and will be obvious to one skilled in the art having this specification before him. Accordingly, this invention is not to be limited except by the appended claims.

The embodiments in which an exclusive property or privilege is claimed are defined as follows:

1. A composition useful as a lubricant comprising

(A) a major amount of a synthetic lubricant base stock which is an ester of a polyol and a C_4 to C_{22} carboxylic acid, and

(B) an oxidation inhibiting amount of a complex alkali metal organophosphorus compound wherein the atomic ratio of alkali metal to phosphorus is at least 0.8:1, said compound being the salt of an alkali metal base and a complex organophosphorus esterification product which is an acid ester of (i) a polyphydric alcohol free of beta-hydrogen atoms, (ii) a C_4 to C_{22} acylating agent, and (iii) a polybasic phosphorus compound selected from the group consisting of (a) free acids of phosphorus selected from the group consisting of phosphoric acid, phosphorous acid and lower alkyl phosphonic acid (b) esters or partial esters of phosphoric acid, phosphorous acid and lower alkyl phosphonic acid and (c) amides of phosphorous acid and phosphonous acid.

2. A composition of claim **1** wherein the polyhydric alcohol free of beta-hydrogen is selected from the group consisting of neo-pentyl, glycol, 2 - butyl-2-ethyl-1,3-propane diol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, and mixtures thereof.

3. A composition of claim **1** wherein the acylating agent is selected from the group consisting of mono- and dicarboxylic acids and acid halides, acid anhydrides and esters of mono- and dicarboxylic acids.

4. A composition of claim **1** wherein the alkali metal base is selected from the group consisting of carbonates, acetates, and hydroxides of K, Na, Li, Cs, and Rb.

5. A composition of claim **1** wherein the atomic ratio of alkali metal to phosphorus in the complex alkali metal organophosphorus compound (B) is from about 1:1 to about 4:1.

6. A composition of claim **1** wherein (B) is present in an amount sufficient to provide at least about 0.01 meq. of titratable base per 20 grams of base stock.

7. A composition of claim **1** wherein the polyol of the base stock is selected from the group consisting of neo-pentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, and mixtures thereof.

8. A composition of claim **1** wherein the polyhydric alcohol is dipentaerythritol, the acylating agent is a fatty acid having from about 4 to about 18 carbon atoms and the polybasic phosphorus compound is phosphorus acid.

9. A composition of claim **8** wherein (B) is present in an amount sufficient to provide at least about 0.01 meq. of titratable base per 20 grams of ester base stock.

10. A composition of claim **8** wherein the alkali metal base is a potassium salt of a weak acid.

11. A composition of claim **10** wherein the ratio of potassium to phosphorus in the complex alkali metal organophosphorus compound is from about 1:1 to about 4:1.

12. A composition useful as a lubricant comprising

(A) a major amount of a synthetic lubricant base stock which is an ester of a polyol and a C_4 to C_{22} carboxylic acid, and

(B) an oxidation inhibiting amount of a complex rare earth metal organophosphorus compound wherein the atomic ratio of rare earth metal to phosphorus is at least about 0.8:1, said compound being the salt of a rare earth metal base and a complex organophosphorus esterification product which is a mixed acid ester of (i) a polyhydric alcohol free of beta-hydrogen atoms, (ii) a C_4 to C_{22} acylating agent, and (iii) a polybasic phosphorus compound selected from the group consisting of (a) free acids of phosphorus selected from the group consisting of phosphoric acid, phosphorous acid and lower alkyl phosphonic acid (b) esters or partial esters of phosphoric acid, phosphorous acid and lower alkyl phosphonic acid and (c) amides of phosphorous acid and phosphonous acid.

13. A composition of claim **12** wherein the rare earth metal is selected from the group consisting of lanthanum, cerium, and praseodymium.

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