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3,567,636

ESTER-BASED LUBRICATING OILS CONTAINING POLYALKYLENEOXIDE-PHOSPHATE ESTERS

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596,402, Nov. 23, 1966, which is a continuation-
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10 Claims

ABSTRACT OF THE DISCLOSURE

A lubricating composition comprising a major proportion of an ester-based lubricating fluid and a minor amount of a phosphate ester or salt thereof of a non-ionic surface active compound, said phosphate ester being selected from the group consisting of mono-esters, di-esters and mixtures thereof, said nonionic surface active compound being the condensation produce of an organic hydroxy compound of from 8 to 50 carbon atoms selected from the group consisting of alkyl phenols and alkanols with at least 1 mole of an alkylene oxide having from 2 to 3 carbon atoms, the nonionic surface active compound containing a maximum of about 50 percent by weight of alkylene oxide based on the weight of the nonionic surface active compound.

This application is a continuation of application Ser. No. 596,402, filed Nov. 23, 1966, which in turn is a continuation-in-part of application Ser. No. 334,917, filed Dec. 31, 1963, both of which are abandoned.

This invention relates to synthetic lubricating compositions and in particular to ester-based lubricants which are characterized by outstanding anti-wear properties, improved viscosity performance, excellent detergency, and outstanding thermal stability and load-carrying capacities. Still further, this invention relates to synthetic ester-based lubricating additives as hereinafter described which impart to the lubricating composition the aforementioned desirable attributes. The primary function of a lubricating composition is, as the name implies, to effect lubricity between moving surfaces and thereby lessen the wear on such moving parts as well as lower power requirements to effect such movements.

In the conventional internal combustion engine, petroleum-based lubricating oils perform generally in a satisfactory manner but the advent of jet engines has created a need for lubricants with properties not possessed by such hydrocarbon lubricants. In jet engines, requirements of low volatility and acceptable viscosity characteristics are generally unattainable with petroleum-based lubricants. As a result of such deficiency in these products, there has been an increasing turn towards the use of synthetic lubricating materials, and particularly ester lubricants which are characterized by improvements in their viscosity characteristics and volatility properties. Since jet engines as well as other mechanical portions of jet aircraft operate over a tremendous range of temperatures from very low to very high temperatures, it is necessary for lubricants employed in such aircraft to function effectively under such adverse conditions of low and high temperature. The lubricants, therefore, must have a high viscosity index in order to provide proper lubrication over such wide temperature variations as well as having low volatility and flash point in view of the extremely high temperatures which are often encountered. While

many of the synthetic ester lubricating oils, and especially those most commonly available, are far superior to petroleum products insofar as viscosity characteristics are concerned, nevertheless there is great room for improvement in these ester lubricating compositions, especially since most of them do not meet the standards of Military Specifications MIL-L-7808D and MIL-L-9236B. While these specifications do not set forth anti-wear requirements, additives having such purposes are not only desired but often absolutely essential in order for the lubricants to be economically and commercially feasible. Numerous materials have been suggested and are being used for improving the wear characteristics of the ester-based lubricants but none of these is known which also contributes to improvements in other of the desirable and necessary properties of such fluids and particularly the viscosity index. Among the most widely employed of the anti-wear additive materials, tricresyl phosphate is probably the most common. This material markedly improves the anti-wear characteristics of the ester-based lubricants but is almost wholly ineffective in improving any of the other properties of the lubricant, and especially the viscosity index.

It has now been discovered that ester-based lubricants of outstanding anti-wear properties and characterized by superior viscosity-index properties may be prepared by the employment in combination with the ester-based lubricant of a particular class of phosphate ester compounds hereinafter to be described.

It is therefore an object of the present invention to provide lubricating compositions which are new and are outstanding in their anti-wear properties.

It is another object of the present invention to provide new and useful lubricating compositions which have superior and unexpected viscosity-index characteristics.

It is still another object of the present invention to provide new and useful ester-based lubricating compositions which are outstanding in anti-wear properties as well as viscosity-index characteristics.

It is still a further object of the present invention to provide new and useful ester-based lubricating compositions which exhibit detergent properties along with excellent viscosity and anti-wear characteristics.

Other objects will appear hereinafter as the description proceeds.

The ester-based lubricating stock which may be employed to produce the compositions of the present invention include any and all of the well-known esters heretofore employed and operable for such purposes, and generally include such esters which range from light to heavy oils and are rated at from about 50 SUS at 100° F. to 250 SUS at 210° F. These esters generally consist essentially of carbon, hydrogen and oxygen, although there may be other substituents in minor amounts, such as halogen. The ester may be a simple ester or one having multiple ester groupings, a diester, a polyester or a complex ester. The esters may be prepared from mono- and poly-functional alcohols, both of the aliphatic and aromatic series on the one hand, and carboxylic acids, both mono- and poly-functional of the aliphatic and aromatic series, on the other hand. The preferred esters are those of the aliphatic series wherein a dibasic acid is esterified with the monohydric alcohol to produce a simple diester. Specific suitable esters which are herein contemplated may be found described in the following United States Patents: 2,499,983-4, 2,575,195-6, 2,703,811, 2,705,724, 2,723,286, 2,743,234, 2,798,083, 2,912,458, 3,019,188, 3,026,262, 3,036,005, 3,038,858-9, 3,058,913.

The disclosure in these patents relative to the esters

described therein as suitable for use in producing ester-based lubricants is hereby incorporated in this application by reference thereto. Among specific acids and alcohols which may be used in producing the base ester stock for the lubricating compositions of the present invention, mention may be made of the following:

butyl alcohol
amyl alcohol
hexyl alcohol
heptyl alcohol
n-octyl alcohol
iso-octyl alcohol
nonyl alcohol
decyl alcohol
undecyl alcohol
dodecyl alcohol
tridecyl alcohol
tetradecyl alcohol
hexadecyl alcohol
octadecyl alcohol
2-ethylhexanol
2-ethyl-4-propylheptanol
2-methylpropanol
ethylene glycol
diethylene glycol
triethylene glycol
propylene glycol
1,4-butanediol
1,5-pentanediol
1,6-hexanediol
p-xylylenediol
p-cyclohexylenediol
2-ethyl-1,3-hexanediol
2-propyl-3,3-heptanediol
2,4-diphenyl-1,3-butanediol
polyethylene glycols (M.W. 100-5000)
polypropylene glycols (M.W. 125-5000)
pentaerythritol
trimethylol propane, and the like
hexanoic acids
heptanoic acids
lauric acid
stearic acid
succinic acid
adipic acid
suberic acid
sebacic acid
azelaic acid
 α -ethyl suberic acid
 α,α' -diethyl adipic acid
glutaric acid
1,1-cyclohexanediacetic acid
5-octene-1,8-dicarboxylic acid
phthalic acid
hemimellitic acid
3-hexene-2,3,4-tricarboxylic acid
1,3,6-hexane tricarboxylic acid
iso-camphoronic acid
4-methyl-2,4,7-octane tricarboxylic acid, and the like.

Specific esters include:

di(2-ethylhexyl adipate)
di(2-ethylhexyl sebacate)
di(2-ethylhexyl azelate)
disec.-amyl sebacate
diisooctyl adipate
di(1-methyl-4-ethyloctyl) glutarate
di-tetradecyl sebacate
ethyl stearate
di-2-ethylhexylphthalate
dibenzyl sebacate
dicyclohexyl adipate
butyl phthalyl butyl glycolate

2,2,4-trimethyl-1,3-pentanediol dipelargonate
trimethylol triheptanoate, and the like.

The phosphate esters of nonionic surface active agents which are herein contemplated are mono- and diphosphate esters and mixtures thereof. The nonionic precursors for the esters are selected from the group consisting of polyoxyalkylene ethers of alkyl phenols and aliphatic alcohols of at least 8 carbon atoms, said oxyalkylene groups containing from 2 to 3 carbon atoms each. The amount of oxyalkylene groups may vary from about 10% (i.e., derived from the interaction of 1 mole alkylene oxide) up to 50% by weight alkylene oxide. The alkylene oxides or precursors thereof which may be employed to yield the corresponding oxyalkylene groups in the nonionic surface active agent are those which contain from 2 to 3 carbon atoms such as ethylene oxide, propylene oxide, and the like. In addition, it is clear and obvious that mixtures of such oxyalkylating reagents may be used whereby there results in the nonionic surfactant, variations in the oxyalkylene groups.

The nonionic oxyalkylated products which are herein contemplated as precursors for the phosphate esters are well known in the art and are derived from alkyl phenols and aliphatic alcohols of at least 8 carbon atoms and the alkylene oxide as, for example, disclosed in U.S. Pats. 2,213,477 and 1,970,578. The following illustrate some typical suitable phenols and alcohols which may be used to form the corresponding nonionic surface active agents which are precursors for the instantly contemplated phosphate esters:

o-, m-, and p-ethyl phenol
o-, m-, and p-propyl phenol
o-, m-, and p-butyl phenol
p-amyl phenol
pentamethyl phenol
dimethyl phenol
2,4,5-trimethyl phenol
2,4,6-trimethyl phenol
nonyl phenol (nonyl derived from propylene trimer)
dodecyl phenyl (derived from propylene tetramer)
hexadecyl phenol
octadecyl phenol, and the like;

phenols containing a plurality of different alkyl groups, for example:

butyl amyl phenol
butyl hexyl phenol
amyl hexyl phenol
amyl heptyl phenol
ethyl heptyl phenol

as well as phenols containing a plurality of similar alkyls such as, in addition to those above,

di-n-hexyl phenol
diisohexyl phenol
di-n-heptyl phenol
di-n-octyl phenol
diiso-octyl phenol
dinonyl phenol
didodecyl phenol
ditetradecyl phenol
diocta decyl phenol
tri-n-octyl phenol
tri-n-butyl phenol, and the like, and

alcohols prepared from C_8 to C_{50} olefins by the "oxo" process.

The above compounds are then reacted with the alkylene oxide as described above to yield the nonionic surface active agents which are then used to prepare phosphate esters employed in the compositions of the present invention.

The phosphate esters may be prepared by the reaction of 1 mole of P_2O_5 with 2 to 4.5 moles of the nonionic surfactant as described and claimed in U.S. Pat. 3,004,056 by Nunn and Hesse, and U.S. Pat. 3,004,057 by Nunn. As described in the said Nunn and Hesse patent, the reaction between the P_2O_5 and the nonionic polyoxyalkylene ether is conducted under substantially anhydrous conditions and at a temperature below about 110° C. In its preferred form, the reaction is carried out by adding the P_2O_5 gradually, with vigorous agitation to the nonionic surface active agent in liquid form. The reaction is exothermic and cooling is in some cases necessary to keep the temperature below 110° C., since discolored and darkened products tend to be produced above this temperature. The reaction proceeds continuously during the addition of the P_2O_5 and is preferably followed by maintenance of the reaction mixture at ambient temperatures up to 110° C. for an additional period of time after completion of such addition to allow for complete solution of the P_2O_5 and reaction with the nonionic surface active agent.

The following examples illustrate the preparation of such phosphate esters.

EXAMPLE A

2.7 moles of a nonionic surface active compound derived from dinonylphenol condensed with 4 moles of ethylene oxide is reacted with 1 mole of P_2O_5 in the manner described in the examples of U.S. Pat. 3,004,056. The product consists of about equal amounts of mono- and di-ester with about 10–15% unreacted nonionic.

EXAMPLE B

The procedure of Example A is repeated except that the nonionic is a dodecyl phenol plus 2 moles of ethylene oxide condensate.

EXAMPLE C

The procedure of Example A is again repeated employing as the nonionic surface active agent a dinonyl phenol plus 5 moles ethylene oxide (40% ethylene oxide content).

EXAMPLE D

The procedure of Example A is once again repeated employing as the surfactant a dinonyl phenol plus 7 moles ethylene oxide (47% ethylene oxide content).

EXAMPLE E

The procedure of Example A is still once again repeated employing as the nonionic surface active agent dinonyl phenol reacted with 1.5 moles of ethylene oxide to yield a nonionic product containing about 20% ethylene oxide.

EXAMPLE F

The above procedures are again repeated using as the nonionic precursor the condensation product of dodecyl phenol with 1.8 moles of ethylene oxide.

EXAMPLE G

The procedure of Example A is again repeated employing the indicated nonionic compounds and the amounts per mole of P_2O_5 : [e.o., ethylene oxide; p.o., propylene oxide.]

Nonionic:	Moles/mole P_2O_5
(1) Isooctyl alcohol+1 e.o.	2.7
(2) n-Octyl alcohol+2 e.o.	3.5
(3) Nonyl alcohol+3 e.o.	3.5
(4) Nonyl alcohol+2 e.o.	4.2
(5) Decyl alcohol+1.5 e.o.	2.0
(6) Decyl alcohol+2.5 e.o.	2.7
(7) Decyl alcohol+3 e.o.	4.5
(8) Lauryl alcohol+3 e.o.	2.7
(9) p-Ethyl phenol+1 e.o.	2.7
(10) 2,4,6-trimethyl phenol+3 e.o.	4.5
(11) p-Amyl phenol+2.5 e.o.	3.0

Nonionic:	Moles/mole P_2O_5
(12) o-Butyl phenol+2 e.o.	2.7
(13) Nonyl alcohol+2 p.o.	2.7
(14) Decyl alcohol+2 p.o.	4.0
(15) Lauryl alcohol+3 p.o.	2.7
(16) p-Butyl phenol+1.5 p.o.	2.7
(17) di-n-Butyl phenol+3 p.o.	2.7
(18) Dodecyl phenol+5 p.o.	2.7
(19) Dinonyl phenol+6 p.o.	2.7
(20) Dinonyl phenol+5 p.o., then 3 e.o.	2.7
(21) Dinonyl phenol+3 p.o., then 3 e.o.	4.5

The chemical construction of the products produced in the above-described examples will usually be about 20–50% of the secondary phosphate ester of the nonionic agent, 30–80% of the primary phosphate ester, and 0–40% of unreacted nonionic agent.

By carrying out the above reaction in the presence of a small amount of a phosphorus-containing compound selected from the group consisting of hydrophosphorous acid, salts of hydrophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid, preferably sodium hypophosphite or hypophosphorous acid, as described in said Nunn 3,004,057 patent, lighter-colored or substantially colorless reaction products are obtained.

While the presence of unreacted nonionic is not detrimental to the attainment of the objects of the present invention, the amount of nonionic can be reduced, if desired to a minimum of less than about 10% by incorporating in the reaction mixture a small amount of mineral acid such as phosphoric acid, hydrochloric acid or sulfuric acid. Since phosphorous pentoxide yields phosphoric acid in the presence of water, the latter can advantageously and preferably be used to form the acid "in situ." With the use of the mineral acid the amount of phosphorous pentoxide can also be increased to as much as 3 moles per mole of nonionic reactant, thereby favoring the formation of the monoester in major amounts, i.e., substantially no diester.

Monoesters and diesters can also be prepared from the corresponding triesters by reacting the triester with phosphoric acid. By varying the ratio of nonionic to acid, one can prepare either mono- or diester to the substantial exclusion of the other. A high ratio of triester to acid (2:1) produces diester whereas a low ratio (0.5:1) produces monoester.

EXAMPLE H

Equimolar amounts of the nonionic surface active compound of Example A and phosphorous pentoxide are heated at 90° C., while adding in the presence of about 0.4% water the P_2O_5 over a period of one hour. Then the reaction mixture is heated for four hours at 125° C. The final product is a monoester.

EXAMPLE I

Example H is repeated employing one mole of a dodecyl phenol plus 2 moles ethylene oxide condensate and 2 moles of P_2O_5 . The final product is a monoester.

EXAMPLE J

Example H is again repeated using the following nonionics:

- (A) isooctyl alcohol + 1 mole ethylene oxide
- (B) nonyl alcohol + 3 moles ethylene oxide
- (C) lauryl alcohol + 3 moles ethylene oxide
- (D) p-butyl phenol + 2 moles ethylene oxide
- (E) p-ethyl phenol + 1 mole ethylene oxide
- (F) octadecanol + 3 moles ethylene oxide
- (G) hexadecanol + 4 moles ethylene oxide
- (H) 1-eicosanol + 6 moles ethylene oxide
- (I) 1-dotriacontanol + 7 moles ethylene oxide
- (J) dodecyl phenol + 5 moles ethylene oxide
- (K) hexadecyl phenol + 3 moles ethylene oxide
- (L) tri-n-octyl phenol + 4 moles ethylene oxide
- (M) tri-n-octyl phenol + 5 moles propylene oxide

(N) dodecyl phenol +3 moles propylene oxide
 (O) dinonyl phenyl +1.5 moles propylene oxide
 (P) diisohexyl phenol +2 moles propylene oxide
 (Q) tri-n-butyl phenol +2 moles propylene oxide
 (R) tri-n-butyl phenol +3 moles propylene oxide
 (S) tri-n-butyl phenol +4 moles propylene oxide
 (T) tri-n-butyl phenol +3 moles ethylene oxide
 (U) hexadecanol +3 moles propylene oxide
 (V) octadecanol +4 moles propylene oxide
 (W) butyl hexyl phenol +4 moles ethylene oxide
 (X) ethyl heptyl phenol +5 moles ethylene oxide
 (Y) ethyl heptyl phenol +3 moles propylene oxide
 (Z) ceryl alcohol +3 moles ethylene oxide
 (AA) 1-octacosanol +4 moles ethylene oxide
 (BB) 1-nonacosanol +7 moles ethylene oxide
 (CC) 1-triacontanol +6 moles ethylene oxide
 (DD) 1-tetratriacontanol +5 moles ethylene oxide
 (EE) 1-tetratriacontanol +2 moles propylene oxide

EXAMPLE K

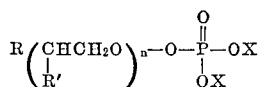
A phosphate triester of the nonionic compound of Example A is prepared by reacting 3 moles of said nonionic with 1 mole of phosphorus oxychloride in the presence of 1 mole of pyridine and 100 ml. of benzene. The POCl_3 is added dropwise to the other components at a temperature of about 0°C . and the temperature is held below 10°C . After all of the POCl_3 has been added, the mixture is refluxed for 3 hours and then the solvent is removed under vacuum distillation. The triester results.

The triester is converted to a monoester by adding 1 mole of phosphoric acid to 0.5 moles of the triester at about room temperature. The monoester results.

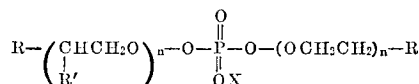
EXAMPLE L

Example K is repeated except that 2 moles of triester are used in lieu of 0.5 mole. The diester results.

The mono- and di-phosphated products used in the present invention may be represented by the following formulae:



and



wherein R' represents H, or methyl; X may be hydrogen, alkali metal, alkaline earth metal, e.g., calcium, magnesium, barium, etc., ammonium, substituted ammonium (e.g., amine); n equals the number of moles of alkylene oxide necessary to yield a final product containing up to 50% by weight of the said alkylene oxide as discussed above; and R is the alcohol or phenol hydrophobe nucleus.

The amount of phosphate ester additive to the ester-based lubricating fluid is not particularly critical, and may vary from about 0.1% to about 10% by weight based on the weight of the ester lubricating fluid although it is preferred to employ from about 1 to 10% by weight.

The following examples will serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

EXAMPLE 1

To 97.0 grams of di-2-ethylhexylsebacate are added 3.0 grams of the barium salt (pH=7.0) of the phosphate ester of Example D. The mixture is heated to 65°C . with stirring until homogeneous in appearance. A similar preparation is made containing 3 grams of tricresyl phosphate. Viscosity measurements are made and anti-wear properties ascertained in a Brown modified Shell Four Ball machine using four steel balls SAE 52-100 as described in U.S. Pat. 3,036,072. The tests are run at 200°F ., 600 r.p.m. at loads of 10 and 40 kilograms. The fol-

lowing Tables I and II list the results obtained with the two formulations and the unmodified sebacate.

TABLE I.—VISCOSITY

5	Composition	KV, ¹	KV,	KV,	Pour	
		210° F.	100° F.	-65° F.		point, ° F.
				VI ²		
	1. Di-2-ethyl hexyl sebacate-----	3.41	12.44	7,868	165	<-65
	2. Di-2-ethyl hexyl sebacate plus tricresyl phosphate-----	3.42	12.42	10,700	166	<-65
10	3. Di-2-ethyl hexyl sebacate plus barium salt of Example D----	3.78	14.48	8,000	178	<-65

¹ Kinematic viscosity.

² Viscosity index.

TABLE II.—SHELL FOUR BALL TESTS

Composition	Scar diameter (mm.) at 10 kg.	Scar diameter (mm.) at 40 kg.
1. Di-2-ethyl hexyl sebacate.....	0.30	0.70
2. Di-2-ethyl hexyl sebacate plus tricresyl phosphate.....	0.25	0.40
3. Di-2-ethyl hexyl sebacate plus barium salt of Example D.....	0.20	0.30

EXAMPLE 2

Example 1 is repeated using, however, di-2-ethyl hexyl azelate as the ester base. The results are summarized in Tables III and IV.

TABLE III.—VISCOSITY

30 Composition	KV, ¹ 210° F.	KV, 100° F.	KV, -65° F.	Pour point, ° F.
1. Di-2-ethyl hexyl azelate.....	2.96	10.68	6,500	152
2. Di-2-ethyl hexyl azelate plus tricresyl phosphate.....	3.04	10.68	8,500	155
3. Di-2-ethyl hexyl axelate plus barium salt of Example D....	3.20	11.80	8,180	180

¹ Kinematic viscosity.

² Viscosity index.

TABLE IV.—SHELL FOUR BALL TEST

Composition	Scar diameter (mm.) at 10 kg.	Scar diameter (mm.) at 40 kg.
1. Di-2-ethyl hexyl azelate.....	0.40	0.70
2. Di-2-ethyl hexyl azelate plus tricresyl phosphate.....	0.30	0.60
3. Di-2-ethyl hexyl azelate plus barium salt of Example D.....	0.20	0.40

From the above data it is clear that the phosphate ester salt used in the present invention is far superior to the unmodified ester lubricant and the tricresyl phosphate-ester lubricant with respect to viscosity and lubricity characteristics. The compositions of the present invention not only are superior in these properties but also these compositions meet the viscosity specifications of MIL-L-78080, which are:

KINEMATIC VISCOSITY

	° F.
3 centistokes minimum	210
11 centistokes minimum	100
13,000 centistokes maximum	-65

It should be noted that the azelate base fails to meet these specifications at 210°F . and 100°F . and the tricresyl phosphate-azelate combination fails at 100°F . Of further outstanding significance is the fact that the barium salt of Example D as used in Examples 1 and 2 is only 50% active because it is prepared by reacting 50 grams of ester of Example D with 21 grams of barium hydroxide-octahydrate in 50 grams of ester base. The reaction is carried out by heating for two hours at 85°C . with agitation.

This further demonstrates the superior properties of the phosphate esters used in this invention for viscosity control and lubricity, especially since tricresyl phosphate is accepted as an excellent additive for improving the lubricating characteristics of the fluid. Still another added feature of the compositions of this invention lies in the

fact that the flash and fire points of the base esters are not lowered by the additives herein contemplated.

EXAMPLE 3

Example 1 is once more repeated using as the lubricant base, a trimethylol propane fatty acid (C_8 - C_{12} mixture) ester commercially available as Cellulube 2505A. In Tables V and VI below, appear the viscosity and wear data as determined and reported in the previous examples.

TABLE V.—VISCOSITY

Composition	KV, 210° F.	KV, 100° F.	KV, -65° F.	VI
1. Cellulube 2505A.....	3.95	16.0	10,200	162
2. Cellulube 2505A plus 3 percent tricresyl phosphate.....	3.74	15.50		151
3. Cellulube 2505A plus 3% barium salt of Example D (50% active).....	4.16	17.52		168

The poor point in each instance is below -65° F.

TABLE VI.—SHELL FOUR BALL TESTS

Composition	Scar diameter (mm.)	
	At 10 kg.	At 40 kg.
1. Cellulube 2505A.....	0.5	0.7
2. Cellulube 2505A plus 3 percent tricresyl phosphate.....	0.2	0.6
3. Cellulube 2505A plus 3% barium salt of Example D (50% active).....	0.2	0.4

EXAMPLE 4

The sonic shear stabilities of compositions containing 1.5%, 3% and 4.5% (100% active) barium salt of Example D in di-2-ethylhexyl azelate are determined in a Raytheon Sonic Oscillator, Model No. DF101, for 30 minutes at 100° F. The results are given in Table VII.

TABLE VII.—SONIC SHEAR STABILITY

Composition	KV before shearing	KV after shearing
1. Di-2-ethylhexyl azelate.....	10.68	10.68
2. Di-2-ethylhexyl azelate plus 1.5% barium salt of Example D.....	11.25	11.28
3. Di-2-ethylhexyl azelate plus 3.0% barium salt of Example D.....	11.78	11.08
4. Di-2-ethylhexyl azelate plus 4.5% barium salt of Example D.....	12.58	12.67

Not only does the additive not decrease the shear stability, but also, as noted, it increases the same somewhat.

EXAMPLE 5

Examples 1, 2 and 3 are repeated employing the following phosphate esters:

- (A) Example A
- (B) Example E
- (C) Example G-4
- (D) Example G-8
- (E) Example G-20
- (F) Example I
- (G) Example J-F
- (H) Example J-N

(I) Example L

Excellent results are obtained in each instance.

EXAMPLE 6

Example 5 is repeated employing the phosphate esters used therein in the form of

- (a) barium salt
- (b) lithium salt
- (c) sodium salt
- (d) ammonium salt
- (e) isopropylamine salt
- (f) triethanolamine salt

The sodium and lithium salts are prepared similarly as the barium salt described above. The others are prepared by reacting equimolar amounts of ammonium hydroxide

or amine slowly at 80-100° C. Then the temperature is raised to 110° C. for about 10-12 minutes to drive off water.

As in the previous examples, the results are excellent and outstanding.

While in the above examples there have been illustrated various metal salts and ammonium salts as well as specific amine salts, it is to be clearly understood that the phosphate esters herein disclosed may be used in the form of any alkali metal salts, any alkaline earth metal salts, and any amine salts, as hereinbefore clearly pointed out, and in addition to those specific amine salts which have been exemplified, mention might also be made of the general class of monoamines and polyamines, both aliphatic and aromatic in nature, and most particularly the monoamine salts of the aliphatic series having up to about 50 carbon atoms in the structure thereof. In addition to the typical aliphatic amines which are monofunctional, such as isopropylamine, octylamine, decylamine, octadecylamine, and other aliphatic amines such as are derived from naturally-occurring materials such as tallow, hydrogenated tallow, coconut oil, soya oil and the like, it is particularly advantageous to employ multi-functional compounds wherein the amino group comprises the salt-forming moiety and the other functional groups include such diverse grouping such as hydroxy, carboxy, sulfonic acid and the like.

Among the latter group of compounds, the alkanol amines are particularly preferred and these include, as merely illustrative, monoethanolamine, diethanolamine, monopropanolamine, monobutanolamine, N-ethyl-monoethanolamine, as well as homologues of the latter which are generally characterized as the N-alkylated mono-alkanolamines.

In addition to the remarkable anti-wear properties, viscosity-index-improvement characteristics, and shear stability of the lubricant compositions of the present invention, mention has also been made of the excellent detergent characteristics of the phosphate esters used herein and of the resultant combinations with synthetic ester bases. The following example demonstrates this improved feature.

EXAMPLE 7

The ester bases of Examples 1, 2 and 3 are used for 3,000 miles in an engine and the sediment is measure. This is compared with the same lubricant to which phosphate ester has been added as in Examples 1, 2 and 3. With the additive there is practically no sediment and the lubricant appears opaque. Without additive, the sediment readily separates and the lubricant is clear above the sediment. On a relative basis the untreated lubricants give sediments from 1.0 to 3.0 ml. whereas with additive the sediment is less than 0.1 ml.

Other variations in and modifications of the described process which will be obvious to those skilled in the art can be made in this invention without departing from the scope or spirit thereof.

I claim:

1. A lubricant composition consisting essentially of an ester-based lubricating fluid in major proportions and about 0.1% to 10%, based on the weight of said fluid, of a phosphate ester, in the form of its free acid or alkali metal, alkaline earth metal or ammonium salt, of an oxyalkylene ether of an organic hydroxy compound containing 8 to 50 carbon atoms and selected from the group consisting of alkylphenols and aliphatic alcohols, said phosphate ester being a monophosphate ester, diphosphate ester or mixture thereof, said oxyalkylene ether containing 1 to 7 oxyalkylene groups of 2 to 3 carbon atoms each and a maximum of about 50% of such groups based on the weight of said oxyalkylene ether, said phosphate ester being prepared by the reaction of P_2O_5 with a non-ionic surfactant in a ratio of P_2O_5 to non-ionic surfactant of 1:2-4.5.

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2. A composition as defined in claim 1 wherein said organic hydroxy compound is an alkylphenol.

3. A composition as defined in claim 1 wherein said organic hydroxy compound is an aliphatic alcohol.

4. A composition as defined in any one of claims 1 to 3 wherein said oxyalkylene groups are oxyethylene groups. 5

5. A composition of claim 1 to 3 wherein said phosphate ester is employed in the form of its free acid.

6. A composition of claim 1 to 3 wherein said phosphate ester is employed in the form of its alkali metal salt. 10

7. A composition of claim 1 to 3 wherein said phosphate ester is employed in the form of its alkaline earth metal salt.

8. A composition of claim 1 to 3 wherein said phosphate ester is employed in the form of its ammonium salt. 15

9. A composition of claim 1 to 3 wherein said fluid comprises a major amount of di-2-ethylhexyl sebacate.

10. A composition of claim 1 to 3 wherein said fluid comprises a major amount of di-2-ethylhexyl azelate. 20

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