

**[54] SYNTHETIC ESTER LUBRICATING
OIL COMPOSITIONS****[75] Inventors: David S. Bosniack, Edison; Stephen
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Company, Linden, N.J.****[45] Notice:** The portion of the term of this
patent subsequent to June 15, 1988,
has been disclaimed.**[22] Filed: May 11, 1970****[21] Appl. No.: 36,436****Related U.S. Application Data****[63] Continuation-in-part of Ser. No. 836,613, June 25,
1969, Pat. No. 3,585,137.****[52] U.S. Cl.252/32.5, 252/49.8, 252/392****[51] Int. Cl.C10m 3/40, C10m 3/30****[58] Field of Search.....252/32.5, 49.8, 51.5 A, 392****[56] References Cited****UNITED STATES PATENTS**

2,839,468	6/1958	Stewart et al.....	252/32.5
2,723,286	11/1955	Young et al.....	252/56

Primary Examiner—Daniel E. Wyman**Assistant Examiner—I. Vaughn****Attorney—Pearlman and Stahl and Ernest V. Haines****[57] ABSTRACT**

Synthetic ester lubricating oils made from saturated aliphatic monocarboxylic acids and neopentyl polyols and containing small amounts of amine addition salts of acid phosphate esters, aminobenzamides, and neutral phosphate esters.

15 Claims, No Drawings

SYNTHETIC ESTER LUBRICATING OIL COMPOSITIONS

This application is a continuation-in-part of our copending application Ser. No. 836,613, filed June 25, 1969 now U.S. Pat. No. 3,585,137.

DESCRIPTION OF THE INVENTION

Turbine engines are customarily employed in aircraft today. They are, however, subjected to extreme temperatures and excessive corrosion difficulties which in turn have adverse effects on the bearings and seals employed in such engines. Alloyed bearings are customarily used in such engines and the rubber seals (usually synthetic) which are employed to retain the oil in the bearing compartments are also subjected to extremes of temperatures which conditions necessitate the employment of highly specialized synthetic ester oils. Heretofore, these oils have been improved by the use of minor amounts, i.e. of the order of 0.01 up to as high as 5.0 wt. percent of various special purpose additives, in an effort to improve the performance of the synthetic ester oils. The severity of operating conditions far exceeds those encountered in internal combustion automotive engines. It has not been advantageous to lubricate aircraft turbine engines using mineral oil compositions. In the past, synthetic ester oils have performed far more satisfactorily but because of the severe operating conditions encountered, such ester base oils, without further compounding, likewise tend to rapidly decompose, corrode metals, and attack synthetic rubber oil seals even though improved metal alloys and oil seals are now conventionally employed. Consequently, it is customary to add small amounts of antioxidants, antiwear or high load reagents, metal passivators, anticorrosion agents, and the like, for the purpose of further improving these oils for their intended aviation turbine engine use.

Many types of synthetic neutral saturated carboxylic acid esters are conventionally employed as turbine engine aviation lubricants. One of the problems presently being encountered is in manufacturing or compounding a synthetic ester lubricant which will be able to withstand even harsher operating conditions than have heretofore been encountered, namely, in lubricating those turbine engines which are to power aircraft designed to fly at supersonic speeds. The instant invention is directed to the compounding of certain specific ester type oils which will satisfy the exacting requirements of such usage.

Heretofore, the synthetic neutral saturated carboxylic acid ester lubricants have employed phenothiazine or the nuclearily substituted C_1-C_{12} alkyl derivatives thereof as an antioxidant, see U.S. Pat. No. 3,218,256, column 2, as well as British Pat. No. 824,114, which latter mentioned patent also shows the use of benzotriazole in such capacity with or without the use of phenothiazine. Additionally, amine antioxidants as shown in column 3 of U.S. Pat. No. 3,247,111 have been employed in conjunction with the phenothiazine and benzotriazoles for the purpose of inhibiting the undue rapid oxidation of such synthetic ester oils. Phenolic antioxidants have been employed as well. Quinizarin and its simple derivatives and analogous compounds are also employed as antioxidants, see U.S. Pat. No. 3,247,111, column 4, lines 3-10. Still further

additives have been employed to act as metal corrosion inhibitors or passivators, such as sebacic acid, as shown by British Pat. No. 928,798 and U.S. Pat. No. 2,730,871. All of the aforementioned types of additives are conventionally used at the present time and the finished oils made in accordance with the present invention will also contain most if not all of them.

The load carrying additives which have been employed are generally the phosphate esters and phosphite esters; see, for example, U.S. Pat. Nos. 2,971,912, column 6; 3,215,720, column 1; and 3,247,111, column 4. In particular, dibutyl phosphite and tricresyl phosphate have been widely used for the purpose of imparting antiwear or load carrying characteristics to the synthetic ester oils although any of the specific materials mentioned in the last three stated U.S. patents are also applicable conventionally for imparting load carrying properties to such oils. Specifically, tris (2-ethylhexyl) phosphate ester, tris (butoxyethyl) phosphate ester and tris (beta chloroethyl) phosphate ester have been used. Other triaryl, trialkaryl and trialkyl neutral phosphates have been employed for imparting load carrying and antiwear properties to such oils, such as tricresyl phosphate, triphenyl phosphate, methyl, di-tertiary butyl phosphate, tri(n-butyl)phosphate, triethyl phosphate, tri-n-hexyl phosphate, tri-o-tolyl phosphate, tri-xylyl phosphate, and tricyclohexyl phosphate. U.S. Pat. No. 3,247,111 at column 4, shows various trihydrocarbyl neutral phosphate and phosphite esters which have heretofore been employed as load carrying and antiwear agents. Other specific phosphorous esters are enumerated in the aforementioned three U.S. patents as improving the antiwear or load carrying ability of various synthetic ester based oils. In the present invention, however, the compounded ester oils contain phosphorous compounds wherein the phosphorous exists only in its highest valence state and the phosphite esters are not used at all. The amine antioxidants, as also shown in column 3 of U.S. Pat. No. 3,247,111, most often are N-phenyl alpha naphthylamine, N-phenyl beta naphthylamine or p,p'-di-isooctyl diphenylamine, although any of the aromatic amines mentioned therein (lines 36-48) may be used in the instant novel oil compositions. The disclosures of the aforementioned patents are incorporated hereinto by reference.

Although Stewart et al, Pat. No. 2,839,468, deals with the use of synthetic lubricants, they are not of the ester type but are rather alkyl ethers of glycols. This patent does show, in column 5, the use of extreme pressure additives, in minor amounts, which additives are the alkyl amine addition salts of alkyl acid phosphates and blends of such salts with free alkyl acid phosphates. Many of these amine addition salts of alkyl acid esters of phosphoric acid contain from 10 to 16 carbon atoms in the primary amine alkyl chain and have been employed in the base oils of the ether type for the purpose of improving the extreme pressure properties of the synthetic oil. Additionally, this patent shows the use of minor amounts of the neutral trialkyl or neutral triaryl phosphates as heretofore referred to for their antiwear properties. Metal passivators or deactivators such as quinizarin and alizarin are also shown in this patent as being conventionally employed.

U.S. Pat. Nos. 2,801,968, 3,247,109 and 3,251,771 disclose somewhat similar additives for synthetic oils including diester oils. Additionally, British Pat. No. 1,180,390 discloses synthetic ester lubricating oils containing a minor amount of a neutral amine addition salt of dibutyl acid phosphate, the specific amine being lauryl amine. This additive is always used in conjunction with a phosphate ester (dicyclohexyl phosphite or dibutyl phosphite), a metal passivator, a neutral trihydrocarbyl phosphate and a lead corrosion inhibitor such as propyl gallate.

The synthetic neutralized saturated carboxylic acid ester lubricating oils which serve as the base oil and to which one or more of the aforementioned additives are added may be of several kinds. Numerous patents disclose these types of ester base oils as being conventionally produced and used as shown by the following patent Nos.: 1,993,736; 2,249,768; 2,766,273; 2,015,088; 2,723,286; 2,743,234; 2,575,196; 3,218,256; 3,360,465 and British Pat. No. 1,025,294, pages 15 and 16.

The specific type of ester base oils to which the present invention relates are the diester, triester and tetraester lubricating oils. These are conventionally produced and marketed for use in turbine engines that power aircraft. These engines are of the "turbo jet," "turbo prop," "turbo fan" and "supersonic jet transport" types. Because these engines and drive mechanisms for powering aircraft are all operated under extremely wide temperature ranges, the use of synthetic ester oils is presently an absolute necessity.

Briefly, these types of esters, as referred to in the above patents, can be described as being formed in the following manner. The diester, triester and tetraester types are formed by reacting di, tri and tetra hindered polyols such as neopentyl glycol, trimethylol propane, trimethylol ethane, and higher trimethylol alkanes, pentaerythritol or dipentaerythritol and so forth, with a C₄-C₁₂ normal or branched chain aliphatic monocarboxylic acid or mixtures of two or more of such acids. These acids are exemplified by n-butanoic acid, valeric acid, pivalic acid, caproic acid, heptanoic acid, caprylic acid, 2-ethyl hexanoic acid, pelargonic acid, lauric acid and the like. The hexaesters of dipentaerythritol are also useful alone or admixed with the aforementioned tetraesters of monopentaerythritol. Either the pure mono, pure di, or mixed pentaerythritols are used. One commercially available technical grade monopentaerythritol contains as much as 10-15 percent of the dimer form and may be used as the alcohol reactant as marketed. The polyesters employed as base oils in the novel compositions hereinafter described are formed from polyols in which the beta carbon atoms thereof contains no hydrogen atoms attached thereto. These are referred to as hindered alcohols. The polyesters formed from non-hindered alcohols have an inherent thermal stability of about 100° F. lower than similar esters formed from the hindered alcohols.

The synthetic ester oils or blends thereof generally have physical properties and specifications as follows: a viscosity index of at least 100, a pour or freezing point not exceeding -40° F., a boiling or decomposition temperature of at least 500° F., a Cleveland Open Cup Flash Point of at least 400° F., and a kinematic viscosity of less than 10 centistokes at 210° F. The supersonic

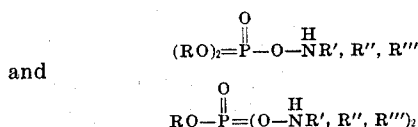
turbine engine oils have a more exacting specification and requirement. These specifications are: a viscosity index of at least 100, a pour or freezing point not exceeding -45° F., a boiling or decomposition temperature of at least 600° F., a Cleveland Open Cup Flash Point of at least 450° F., and a kinematic viscosity of less than 5.5 centistokes at 210° F. The novel combination of additives incorporated into the synthetic ester oils in accordance with the presently discovered advance in the art is applicable to the more generally used synthetic aviation ester oils of less exacting specification as well as to the more exacting requirements of the supersonic aviation turbine ester oils.

It has now been discovered that in those instances where the trihydrocarbyl neutral phosphate esters alone are employed in synthetic ester oils for the purpose of improving their load carrying or antiwear properties, such has not been found to be the case when measured by the Ryder Gear Test. In fact by such a test, such neutral esters do not impart the desired load carrying properties to the ester oils. These neutral phosphate esters are extremely beneficial, however, because they tend to passivate metals and to reduce the viscosity and acidity buildup in the ester oils during their use. However, an effective load carrying agent is also necessary. It has now been discovered that in conjunction with the use of neutral phosphate (triesters), amine neutralized addition salts of one or more acidic phosphate esters of between about 14 and about 60 carbon atoms per salt molecules are efficacious for imparting the requisite load carrying properties to such oils. Amine neutralized mono- and/or di-phosphate esters whose molecules contain less than 14 carbons are not suitable because the synthetic silicon-containing elastomeric seals are readily attacked both from the standpoint of deterioration and shrinkage. In turbine engines synthetic elastomeric seals such as silicone and fluorosilicone rubbers are widely employed. All of the phosphorus containing additives employed in the synthetic ester oils are either neutral (triesters) or are neutralized with an amine (mono and/or dihydrocarbyl ester neutralized with the required number of mols of amine) and, in addition, all of the phosphorus containing additives contain the phosphorus in its highest valence state, i.e. the phosphorus in the compounds used is in the fully oxidized state. Furthermore, the phosphorus containing additives must possess at least sufficient oil solubility so that the required or desired amounts thereof will be dissolved in the synthetic ester oil. Thus, a hydrocarbyl amine of low number of carbon atoms may be used to neutralize a hydrocarbyl acid phosphate ester of a high number of carbon atoms or a hydrocarbyl amine of a high number of carbon atoms may be used to neutralize a hydrocarbyl acid phosphate ester of a low number of carbon atoms. In general, the total number of carbon atoms of the amine moiety or moieties should be at least a total of 4 per amine phosphate molecule and the total number of carbon atoms of the acid phosphate ester should be at least 1 if a phosphate mono-ester, at least 2 if a phosphate di-ester, and at least 1.5 (average), if a mixed mono- and diphosphate ester; provided, however, that the sum total of carbon atoms of the amine moiety or moieties plus those of the acid phosphate ester moiety is at least 14 carbon atoms per molecule of the neutral amine acid addition salt.

As used in this description and accompanying claims, the term "hydrocarbyl" is intended to include not only a monovalent hydrocarbon radical of aliphatic, aromatic or mixed character but also includes the simple derivatives thereof such as the hydroxy or chloro hydrocarbyls as well.

Only certain of the long chain normal, or branched, alkyl primary, secondary, or tertiary amine addition salts of mono or dihydrocarbyl acid phosphate esters or mixtures of such esters are useful. For example, the total number of carbon atoms per molecule in the amine neutralized acid phosphate ester must be at least 14 and up to 60 carbon atoms, preferably contains between about 18 and about 60 carbon atoms per molecule. Such neutral amine addition salts, in some cases do to some slight extent, result in an attack on the silicon-containing elastomeric seals but they do not nullify or eliminate the desirable properties of the neutral phosphate esters. The addition of minor amounts, i.e., of the order of 0.01-1.0 wt. percent of such neutral amine salts of the acid phosphate esters, does materially contribute to the load carrying and antiwear properties of the ester oil, in measurable amounts, and in addition these neutral amine salts impart inhibition and anticorrosion properties to the oils employed in turbine engines in modern day usage. The greatest effectiveness of these defined amine salts as contrasted with similar salts excluded from the above definition is to be found where the seals are fabricated from the commercially available silicone and fluorosilicone elastomers.

In general, the mono, di, or mixed mono and di-acid phosphate ester amine addition salts may be represented by the formulas:



wherein R is a hydrocarbyl radical of from one to 18 carbon atoms, and R', R'', and R''' are each hydrogen or hydrocarbyl of from about one to about 24 carbon atoms, at least one of the R', R'' and R''' being a hydrocarbyl group and the amine acid addition salt of the acid phosphate ester containing a total of between about 14 and about 60 carbon atoms per molecule, regardless of which acid phosphate ester (or mixtures thereof) is used. If a diphosphate ester is employed, only one mole of the amine is employed per mole of ester but if a monophosphate ester is employed, there will be two acid hydrogen atoms, both of which are to be neutralized with amine. Hence, two moles of monoamine would be employed or if a diamine is employed, at least two primary, secondary, or tertiary amino groups per molecule of acid ester would be employed so that in all events, all acid phosphate hydrogens are completely neutralized with amino groups. Thus, if the acid phosphate employed is dimethyl acid phosphate, this would be neutralized with, for example, a normal or branched chain alkyl amine mole for mole; if the acid phosphate ester employed were monomethyl phosphate, this would be

neutralized with two moles of an iso or branched chain alkyl amine per mole of acid phosphate employed; and finally, if a mixture of mono and dimethyl acid phosphate ester were employed, sufficient of the alkyl amine would be employed to insure complete neutralization of the acid hydrogen groups of both the mono and dialkyl acid phosphate ester mixture. In the following examples and the data appearing in the tables, in almost all cases, mixed acid phosphate esters were employed because, commercially, such mixtures are available but in all cases where a mixture of mono and dihydrocarbyl acid phosphates were employed, the range of carbon atoms shown in the following Tables have been estimated (50-50 mixture of mono and diesters) and are on a computed basis, with the range of carbon atoms per molecule ranging from a computation based on the dihydrocarbyl phosphate ester as one limit of the total carbon range and the monohydrocarbyl acid phosphate ester as the other limit of the total carbon range. Also, the long chain amines used were also, in fact, mixtures of various chain length alkyl primary amines. Here, too, average chain lengths were used. Furthermore, in all cases in preparing the amine neutralized acid addition salts of the acidic phosphate esters, these esters were dissolved in 95 percent ethyl alcohol and sufficient amine was added thereto to give a pH to the solution of 7.5 after which the solvent was removed by simple distillation and the product was stripped to 140° C. under one millimeter of mercury, vacuum.

Specific monohydrocarbyl, dihydrocarbyl, or hydroxy hydrocarbyl derivatives of acidic phosphate esters and mixtures thereof which may be employed and which may be neutralized with amine to form the corresponding acid addition salts are listed below. They may be alkyl, cycloalkyl, aryl, alkaryl, aralkyl radicals. For the most part, only the monoesters are listed but it is to be understood that either the monoester or the corresponding diester may be used alone. In general, the commercially available materials comprise a mixture of both the mono- and dihydrocarbyl acid phosphate esters. Where the mono esters are stated, it is intended that diesters or mixtures of mono and diesters are to be included as well. Some of the specific acid phosphate esters which may be employed and which are representative of the types of phosphate esters that can be used in preparing the additives employed in the present invention are as follows: methyl acid phosphate, ethyl acid phosphate, n-propyl acid phosphate, isopropyl acid phosphate, n-butyl acid phosphate, isobutyl acid phosphate, amyl acid phosphate, isoamyl acid phosphate, n-hexyl acid phosphate, isohexyl acid phosphate, cyclohexyl acid phosphate, normal or branched long chain alkyl acid phosphates such as decyl, dodecyl (lauryl), stearyl, and the like; methyl phenyl acid phosphate, n-butyl tolyl acid phosphate; aryl phosphates such as phenyl or naphthyl acid phosphates, the alkaryl acid phosphates such as ortho, meta or para tolyl acid phosphates, cresyl acid phosphate, ortho, meta or paraethylphenyl acid phosphates, o,m,p.-octyl phenyl acid phosphates and o,m,p.-nonyl phenyl acid phosphates and the aralkyl acid phosphates such as benzyl acid phosphate and phenethyl acid phosphate.

The primary, secondary or tertiary amines which may be employed are alkyl, aryl, alkaryl, or aralkyl amines in which the alkyl radicals or the alkyl portion of the radicals are either of straight chain or branched chain character and contain from one to 24 carbon atoms per hydrocarbyl radical. Representative alkyl radicals whether of a mono primary alkyl amine, a dialkyl secondary amine or trialkyl tertiary amine or mixtures thereof have alkyl radicals such as methyl, ethyl, propyl, butyl, amyl, cyclohexyl, lauryl, myristyl, cetyl (palmityl), stearyl, arachidyl, behenyl, lignoceryl, and cerotyl. Phenyl, naphthyl, benzyl and dibenzyl amines as well as the corresponding phenethyl amines are also suitable to use. Methyl, phenyl amine; butyl, tolyl amine, o,m, or p,-dodecylphenylamine, o,m, or p,-nonylphenylamine, and the like are examples of useful mixed alkyl, aryl and alkaryl amines. Many of these materials are commercially available as mixtures, such as amines derived from C_{12} oxo alcohol bottoms. For example, a mixed branched chain C_{12} — C_{14} primary aliphatic amine composition is sold under the tradename "Primene 81-R" and a mixed branched chain C_{16} — C_{22} primary amine composition is sold under the tradename "Primene JMT." Each of these was used in preparing some of the salts employed in securing the data appearing in the following tables. Many of the amine mixtures sold under the Armeen trademark are likewise suitable compositions to be employed in producing the amine acid addition salts. These contain alkyl radicals ranging from C_{12} through C_{18} or mixtures thereof which are derived from fatty acids. The corresponding C_2 — C_{20} poly alkylene polyamines are also useful.

The formation of the amine addition salts of the acid phosphate esters is quite simply carried out. Generally, because of the relatively high molecular weight of some of the amines and of some of the acid phosphates that are solids at normal or atmospheric temperatures, they may be reacted under elevated temperatures of say 120° to as high as 160° C. or they may be reacted as solutions at ambient temperatures in organic solvents in forming the acid addition salts. Suitable solvents are the hydrocarbon solvents such as naphtha, benzene, toluene, pentane, hexane, petroleum ether, or the lower alcohols such as ethanol, isopropanol, butanol, the ester base oils, amyl acetate and other conventional carboxylic acid ester solvents, and the like. The amine addition salts of the acidic phosphate esters may also be formed in situ by the separate additions of the two reactants directly to the base oil. Sufficient amounts of the primary, secondary or tertiary amines, or mixtures thereof, maybe employed so as to give a pH of the reaction mixture of slightly less than 7.0, i.e., 6.5, but preferably a pH of at least 7.0 is used in order to insure that for the most part the acid phosphate esters are neutralized. Usually, sufficient amine is incorporated into the reaction mixture to give a final pH of about 7.5. If less amine is used, the reaction mixture will comprise a mixture of unreacted phosphate esters and the amine addition salt of phosphate esters. If more than the amount of amine reacted to give a pH of 7.0–7.5 is used, then, of course, the reacted mixture will comprise a mixture of free amine and the amine acid addition salt of the acid phosphate ester. After the required amount of amine has been added to the acid phosphate reaction

mixture, and thorough agitation has insured a completion of the reaction (neutralization), the solvent, if used and not an ester base oil, may be stripped from the reaction mixture while distilling the same therefrom. This conveniently is accomplished under a vacuum, i.e., 1–5 millimeters of mercury vacuum.

The amount of amine acid addition salt incorporated into the synthetic neutral ester lubricant base stock generally varies between about 0.01 and about 5.0 parts per 100 parts by weight of the base ester oil. Preferably, about 0.1 to about 0.5 parts of the additive is employed. The amount of trihydrocarbyl neutral phosphate ester used is between about 0.01 and about 10.0 parts, preferably between about 0.1 and about 5.0 parts per 100 parts of base oil.

In the following runs, tests were conducted on representative synthetic ester lube oils using various phosphates, acid phosphates and amine neutralized acid phosphates and, inter alia, standard Ryder Gear Tests were carried out on such compounded oils. The Ryder Gear Test is a standard test and is identified as FTM-STD 791 Method 6508 (MIL-7808C). In some instances, additional elastomer seal swell tests were used as well as the Ryder Gear Test and was the only test carried out with respect to certain compositions. This test is a standard test and the rubber employed was a fluorosilicone rubber or a silicone rubber. This test is identified in MIL-L-7808 G and is a standard test for determining the percentage of swell or shrinkage of various synthetic rubbers which are customarily employed in turbine engines particularly aviation turbine engines. The IAE Gear Load Test is a British standard test and is a requirement of the Directorate of Engine Research and Development 2487 and 2497 specifications.

In the following tests, the following base oils were employed. In all cases, the amount of base oil used was 100 parts by weight and the additives used were also on a weight basis.

Oil A — A tetraester of pentaerythritol with a mixture of C_4 — C_7 normal alkanolic acids.

Oil B — A tetraester of a mixture of 90 percent monopentaerythritol and 10 percent dipentaerthritol fully esterified with a mixture of C_5 — C_{10} normal alkanolic acids.

Although the blended or compounded polyester synthetic ester oils as the final compositions to be used in aviation turbine engines have as their base oils, oils of the types represented by Oils A, and B, and although the improvement in the performance of these oils is largely attributable to the use of neutral phosphate esters in conjunction with the heretofore described amine addition salts of acid phosphate esters, all phosphorus compounds containing phosphorus in its highest valence or oxidative state, nevertheless, the novel anthranilamides as described and claimed in our copending parent application Ser. No. 836,613 now U.S. Pat. No. 3,585,137 together with the use of conventional additives as detailed in that application or as referred to therein by reference to U.S. Patents are also intended to be used in the same manner and for the same purposes in the instant novel synthetic ester oil compositions. No phosphite esters, neutral or acidic, are however, to be incorporated into the instant compositions. The usual amine or phenolic antioxidants,

the phenothiazines or phenothiazine per se, the trace amounts of quinizarin and sebacic acid and their art recognized equivalents (antioxidants and metal corrosion are inhibitors) incorporated into the instant finished composition, in their usual but recognized amounts.

In the runs shown in Table I, no other additives were incorporated into the base oils except those additives shown in Table I and the rubber swell tests were carried out for a period of 72 hours at a temperature of 302° F. (150° C.).

0.1 parts Quinizarin

0.1 parts anthranilamide

The above formulation is designated in the Table as Oil C. In all tests, the amine addition salt was used and added in the amount of 0.1 parts. This was a mixed iso C₁₂—C₁₄ alkyl primary amine salt of mixed methyl and dimethyl acid phosphate, and in those runs wherein tricresyl phosphate was used the amount used was 1.0 part.

TABLE I

Run No.	Base oil	Primary amine salt acid phosphate additive	Amount, wt. percent	Additive, est. total carbon atoms/mole	Ryder gear load, p.p.i.	Seal swell, fluid loss, cone rubber
1	A	None			2,300	
2	A	i-C ₁₂ —C ₁₄ alkylamine, methyl phosphate	0.1	15-27	2,500	—10.00
3	A	i-C ₁₈ —C ₂₂ alkylamine, methyl phosphate	0.1	22-41	4,326	—2.61
4	A	60% i-C ₁₈ —C ₂₂ alkylamine, methyl phosphate; 40% n-dodecylamine, methylphosphate	0.1	19-35	3,506	—2.78
5	A	i-C ₁₂ —C ₁₄ alkylamine, lauryl phosphate	0.5	37-38	3,196	+1.91
6	A	Tris (butoxyethyl) phosphate	2.0	18	2,980	
7	A	i-C ₁₂ —C ₁₄ alkylamine, butyl phosphate	0.1	21-30		—7.11
8	A	i-C ₁₈ —C ₂₂ alkylamine, butyl phosphate	0.1	28-44		—1.22
9	A	n-dodecylamine, butyl phosphate	0.1	20-28		—0.35
10	A	i-C ₁₂ —C ₁₄ alkylamine, lauryl phosphate	0.1	37-38	2,771	+1.91
11	A	i-C ₁₈ —C ₂₂ alkylamine, lauryl phosphate	0.1	44-52		+3.75
12	A	n-dodecylamine, lauryl phosphate	0.1	36		+3.90
13	A	i-C ₁₂ —C ₁₄ alkylamine, phenyl phosphate	0.1	25-32	2,797	—1.91
14	A	i-C ₁₈ —C ₂₂ alkylamine, phenyl phosphate	0.1	32-46		+1.81
15	A	n-dodecylamine, phenyl phosphate	0.1	24-30		+1.04
16	B*	i-C ₁₂ —C ₁₄ alkylamine, methyl phosphate	0.1	15-27	4,290	—9.73
17	B	i-C ₁₈ —C ₂₂ alkylamine, methyl phosphate	0.1	22-41		—4.85
18	B	Tricresylphosphate	1.0	21		+2.76
19	B	i-C ₁₂ —C ₁₄ alkylamine, methyl phosphate	0.1	15-27	4,071	—8.33
20	B	Tricresylphosphate	1.0	21		
21	B	i-C ₁₈ —C ₂₂ alkylamine, methyl phosphate	0.1	22-41		—3.14
22	B	Tricresylphosphate	1.0	21		
23	B	i-C ₁₂ —C ₁₄ alkylamine, methyl phosphate	0.05	22-41		+3.73
24	B	Tricresylphosphate	1.0	21		
25	B	i-C ₁₈ —C ₂₂ alkylamine, methyl phosphate	0.05	15-27		—5.60
26	B	Tricresylphosphate	1.0	21		

*Base oil B with no phosphate amine salt additive and no neutral phosphate had a Ryder gear load of about 2,800 p.p.i.

From the data shown in Table I, it can be said that the amine addition salts of the acid phosphate esters are primarily functioning as load carrying additives regardless of the total number of carbon atoms per molecule contained therein. See the Ryder Gear Test. However in order to obtain enhanced results with regard to seal compatibility, i.e., no shrinkage or seal deterioration, of the synthetic rubber seals only those amine addition salts that contain an average of at least 14 carbon atoms per molecule and, preferably, wherein the amine portion of the salt contains at least 12 carbon atoms, have proven to have imparted markedly improved qualities in this regard, i.e., no seal destruction, as well as with regard to load bearing qualities, particularly the IAE Test (see Table II). Shrinkage is dangerous because oil can leak past seals. A slight swell is desired, i.e., about 1 to 3 percent, because this insures against leakage of oil past the synthetic rubber seals.

In the following test data as shown in Table II, the base oil used in all instances was as follows (the parts being by weight):

100 parts Oil B

1.6 parts p,p'-diisooctyl diphenylamine

0.4 parts phenothiazine

0.02 parts sebacic acid

TABLE II

run no.	IAE Gear Load, % of Reference Oil (EATO-35)*	oil C	oil C + 1.0 part Tricresyl Phosphate
23	110°C., 2000 r.p.m.	161	beyond capacity of machine to reach termination point
24	110°C., 6000 r.p.m.	145	261
25	Ryder Gear Load, ppi	4,290	4356
26	Seal Swell, Silicone Rubber		
27	200°F./72 hours	+5.30	+4.47
28	225°F./72 hours	+5.73	+3.87
29	225°F./72 hours	+6.12	+4.93
30	250°F./72 hours	+4.89	+4.38
31	250°F./72 hours	+2.69	+2.50
32	302°F./72 hours	+2.71	+2.59
33	302°F./72 hours	+0.52	+0.36
34	Seal Swell, Fluoro-silicone Rubber		
35	225°F./72 hours	+0.08	+0.01
36	302°F./72 hours	—9.50	—9.62

*Described in British Pat. No. 666,697.

Runs 26 and 27, 28 and 29, 30 and 31, and 32 and 33 were duplicate runs as to each pair. The results of both runs in each pair are set forth.

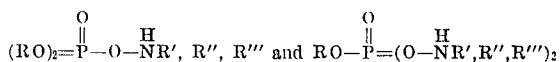
From the data appearing in Table II, it is apparent that insofar as load carrying qualities are concerned, the presence or absence of the neutral phosphate (but the presence of the amine salt acid phosphate) gives

about the same results (Ryder Gear Test). However, the ester oil containing the ester (tricresyl phosphate) shows unusual and unexpected load carrying capabilities on the IAE gear machine test (Runs 23 and 24), which test is a standard and conventional test procedure especially in Great Britain. Also the oil containing the neutral phosphate ester does not deteriorate silicone rubber over the temperature range of 200° to 302° F. But with the use of fluorosilicone rubbers, the oils used in one test run shown in Table II (Run 35) showed some shrinkage and destruction of the rubber at 302° F. which undesired results can be avoided by using C₁₈—C₂₂ alkyl amine addition salt of a C₁₂ alkyl acid phosphate ester. See Run 11 of Table I which used base oil A.

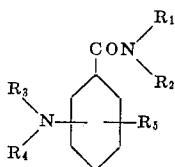
Having now thus fully described and illustrated the present invention, what is desired to be secured by Letters Patent is:

What is claimed is:

1. A lubricating oil composition comprising a major portion, as a base oil, of a synthetic polyester lubricating oil formed by esterifying a hindered aliphatic polyol with a mono aliphatic carboxylic acid or by esterifying mixtures of said polyols with mixtures of said carboxylic acids and an amount, sufficient to improve load carrying properties, of (i) a neutral phosphate ester and (ii) an amine neutralized acid addition salt of a hydrocarbyl acid phosphate ester having at least one of the formulas or mixtures of the formulas:



wherein R is a hydrocarbyl radical of between about one and about 18 carbon atoms, and R', R'' and R''' are each hydrogen or hydrocarbyl groups of from about one to about 24 carbon atoms, at least one of R', R'' and R''' being a hydrocarbyl group, the amine acid addition salt of the acid phosphate ester containing a total of between about 14 and about 60 carbon atoms per molecule, all phosphorus compounds present being neutral and having phosphorus in its highest valence state, said composition also containing an amount, sufficient to inhibit metal corrosion, of an aminobenzamide having the formula:



wherein R₁ and R₂ are each hydrogen, C₁—C₁₂ alkyl, phenyl, phenalkyl or cycloalkyl, R₃ and R₄ are each hydrogen, C₁—C₉ alkyl, C₁—C₁₃ acyl, or phenyl and R₅ is hydrogen, C₁—C₉ alkyl, or halo C₁—C₉ alkyl.

2. A lubricating oil composition as in claim 1 wherein the amine neutralized acid addition salt of a hydrocarbyl acid phosphate ester is one in which the acid phosphate ester is a mixture of mono and dialkyl phosphates and the aliphatic polyol is selected from the group consisting of neopentylglycol, trimethylol

propane, pentaerythritol, trimethylol ethane, dipentaerythritol, trimethylolbutane and mixtures thereof.

3. A lubricating oil composition as in claim 2 wherein the acid phosphate ester is a mixture of mono and dialkyl acid phosphate.

4. A lubricating oil composition as in claim 2 wherein the amine employed in forming the acid addition salt is a mixture of iso C₁₂—C₁₄ alkyl primary amines.

5. A lubricating oil composition as in claim 2 wherein the amine employed in forming the acid addition salt is a mixture of iso C₁₈—C₂₂ alkyl primary amines.

6. A lubricating oil composition as in claim 2 wherein the amine employed is a mixture of iso C₁₈—C₂₂ alkyl primary amine, the acid phosphate is a mixture of mono and di methyl phosphate and the neutral phosphate is tricresyl phosphate.

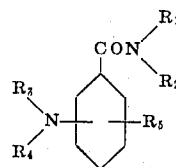
7. A lubricating oil composition as in claim 1 wherein the amount of amine acid addition salt and the amount of neutral phosphate ester are each between about 0.01 and about 10.0 parts per 100 parts of the ester base oil.

8. A lubricating oil composition as in claim 1 wherein the ester oil composition contains (i) between about 0.01 and about 5.0 parts of a C₁₂—C₂₂ alkyl primary amine addition salt of a mixed mono and dialkyl acid phosphate wherein the alkyl of the acid phosphate ranges between about C₁ and about C₁₈ and (ii) between about 0.01 and about 10.0 parts of a trialkaryl phosphate, the ester base oil also containing a small but effective amount of an aromatic amine antioxidant.

9. A lubricating oil composition as in claim 1 wherein the ester oil is a tetraester of pentaerythritol with a mixture of C₄—C₇ n-alkanoic acids.

10. A lubricating oil composition as in claim 1 wherein the ester oil is a tetraester of mixed mono and di pentaerythritol with a mixture of C₅—C₁₀ n-alkanoic acids.

11. A lubricating oil composition comprising a synthetic saturated mono carboxylic acid — hindered polyol ester lubricating oil and minor but effective amounts of an amine neutralized acid addition salt of a hydrocarbyl acid phosphate mixed mono and diester containing at least 22 carbon atoms per molecule, a trihydrocarbyl phosphate, a dialkaryl amine antioxidant, and an amount, sufficient to inhibit corrosion, of an aminobenzamide having the formula:



wherein R₁ and R₂ are each hydrogen, C₁—C₁₂ alkyl, phenyl, phenalkyl or cycloalkyl, R₃ and R₄ are each hydrogen, C₁—C₉ alkyl, C₁—C₁₃ acyl, or phenyl and R₅ is hydrogen, C₁—C₉ alkyl, or halo C₁—C₉ alkyl.

12. A lubricating oil as in claim 11 wherein the trihydrocarbyl is tricresyl phosphate and the ester oil is a fully esterified mixture of mono and dipentaerythritol esterified with C₈—C₁₀ n-alkanoic acids.

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13. A synthetic ester lubricating oil comprising per 100 parts by weight of the polyester of mixed mono and dipentaerythritol, in the weights of mono and dialcohols of between about 80 to 90 wt. percent of mono and about 10 to 20 wt. percent of di, esterified with mixed C_5-C_{10} n-alkanoic acids, about 1.6 parts of p,p'diisooctyl diphenylamine, about 0.4 part of phenothiazine, about 0.1 part each of quinizarin, anthranilamide and the mixed iso $C_{12}-C_{14}$ primarily

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alkyl amine salt of mixed monomethyl and dimethyl acid phosphate esters, about 1.0 part of tricresyl phosphate and about 0.02 part of sebacic acid.

14. The lubricating oil composition of claim 1 wherein R is a methyl group.

15. The lubricating oil composition of claim 11 wherein the hydrocarbyl acid phosphate mixed mono and diester is of methanol.

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