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Jervis et al.

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[54] **LUBRICATING OIL COMPOSITIONS**

[75] Inventors: **Graham James Jervis,** Abingdon; **Robert Robson,** Wantage, both of England

[73] Assignee: **Esso Research and Engineering Company,** Linden, N.J.

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[58] **Field of Search** 252/32.5

[56] **References Cited**

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Primary Examiner—Patrick P. Garvin
Assistant Examiner—Andrew H. Metz
Attorney, Agent, or Firm—Byron O. Dimmick

[57] **ABSTRACT**

A lubricating oil composition having good antiwear and load carrying properties comprises a lubricating oil and a mixture of (a) a quaternary hydrocarbyl ammonium salt of a mono (C_1 – C_4) alkyl dihydrogen phosphate and (b) a quaternary hydrocarbyl ammonium salt of a di-(C_1 – C_4) alkyl hydrogen phosphate, e.g. tetrabutyl ammonium salts of mixtures of methyl hydrogen phosphate and dimethyl hydrogen phosphate.

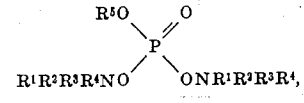
7 Claims, No Drawings

LUBRICATING OIL COMPOSITIONS

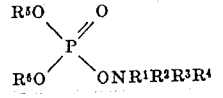
This invention relates to lubricating oil compositions containing amine salts of phosphoric acids.

Lubricating oils usually require additives to improve the anti-wear and load carrying properties of the oil, and this is especially the case for aircraft lubricating oils, e.g. aviation turbine lubricants. Certain amine salts of phosphoric and thiophosphoric acids have been proposed previously as anti-wear additives, but although some show good anti-wear properties they are corrosive and/or incompatible with silicone elastomers. We have now found certain amine salts which not only show good anti-wear or extreme pressure properties, but also have good silicone elastomer compatibility. They also show good corrosion properties.

According to this invention a lubricating oil composition comprises a lubricating oil and a mixture of certain amine salts. This mixture comprises (a) a quaternary hydrocarbyl ammonium salt of a mono (C_1 – C_4) alkyl dihydrogen phosphate of the formula



and (b) a quaternary hydrocarbyl ammonium salt of di-(C_1 – C_4) alkyl hydrogen phosphate of the formula



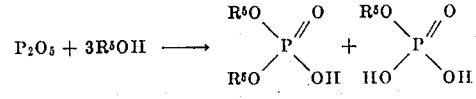
where R^1, R^2, R^3 and R^4 are similar or dissimilar hydrocarbyl groups, R^1, R^2, R^3 and R^4 containing a total of at least 10 carbon atoms, and R^5 and R^6 similar or dissimilar are C_1 – C_4 alkyl groups.

The total number of carbon atoms in R^1, R^2, R^3 and R^4 must be at least 10 and is preferably more, e.g. at least 14. This means that although one or more of the groups can be relatively short chain, e.g. methyl, or ethyl, one or more of the other groups must be long chain, e.g. decyl, dodecyl, etc. When the mixture of amine salts is added to mineral oils the preferred maximum number of carbon atoms in R^1, R^2, R^3 and R^4 is 100, whereas when the mixture is added to synthetic ester oils the preferred maximum number of carbon atoms is 40. Although the groups R^1, R^2, R^3 and R^4 can be different, in practice it is preferred that at least two of the groups be the same, e.g. $R^1 = R^2$ = methyl, R^3 = ethyl, and R^4 = octadecyl; or $R^1 = R^2$ = methyl, and $R^3 = R^4$ = octadecyl. The groups R^1, R^2, R^3 and R^4 may be straight-chain or branched-chain. R^1, R^2, R^3 and R^4 may be alkaryl, aralkyl, cycloalkyl, or aryl, but they are preferably alkyl groups. Thus, one or more of the groups R^1, R^2, R^3 and R^4 may be methyl, ethyl, n-propyl, iso-butyl, n-hexyl, n-decyl, 2-ethyl decyl, n-octadecyl, m-tolyl, p-ethyl phenyl, benxyl, cyclooctyl, phenyl, or naphthyl; provided the total number of carbon atoms in the four groups is at least 10. Particularly preferred cases are where at least three of the groups s R^1, R^2, R^3 and R^4 are the same alkyl groups, e.g. all the same such as n-butyl, or three are octyl as in hexyl trioctyl ammonium salts.

Although each of the groups R^1, R^2, R^3 and R^4 are termed hydrocarbyl groups, they may however be substituted by polar substituents, e.g. chlorine, or bromine atoms or keto or ethereal groups, provided these substituents are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the group; e.g. the groups contain no more than 10% by weight of polar substituent based on the weight of the hydrocarbyl portion of the group.

The groups R^5 and R^6 are alkyl groups containing 1, 2, 3 or 4 carbon atoms, i.e. they are methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, or iso-butyl groups. It is preferred that both R^5 and R^6 are the same, e.g. both methyl groups or both ethyl groups. Particularly preferred salts are mixtures of tetra-n-butyl ammonium salts of di methyl hydrogen phosphate and methyl di hydrogen phosphate and mixtures of hexyl trioctyl ammonium salts of methyl dihydrogen phosphate and dimethyl hydrogen phosphate.

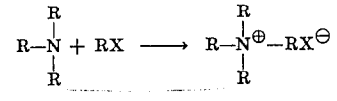
The mixture of acid phosphates from which the quaternary ammonium salts (a) and (b) are derived is best prepared by reacting phosphorus pentoxide with a C_1 – C_4 alcohol or mixture of alcohols, in a proportion of about 3 moles of alcohol per mole of pentoxide. A mixture of alkyl phosphates is obtained according to the following reaction.



In practice the phosphorus pentoxide can be stirred vigorously in dry ether and the alcohol is added dropwise at a rate sufficient to cause the ether to reflux gently. The product may thereafter be filtered to remove any unreacted phosphorus pentoxide, and the ether removed by evaporation under vacuum.

The mixture of alkyl phosphates thus obtained is reacted with a quaternary ammonium hydroxide solution (e.g. 40% aqueous). Such solutions may be conveniently prepared by reacting at ambient temperature a tertiary amine with an alkyl halide to form the quaternary ammonium halide.

e.g.



This halide is mixed with a solution of silver oxide in water, and the reaction mixture is agitated. Silver halide is precipitated and a solution containing quaternary ammonium cations and hydroxide anions is obtained. Alternatively the quaternary ammonium halide can be converted to the corresponding hydroxide by the use of a suitable ion exchange resin, e.g. a polystyrene divinyl benzene copolymer substituted with tertiary amine groups.

On reacting such quaternary ammonium hydroxide solutions with the mixture of alkyl phosphates, the desired mixture of amines salts (a) and (b) is formed. The mole ratio of (a) to (b) prepared by these methods is approximately 1:1, and this is the preferred ratio.

The amount of the amine salt mixture added to a lubricating oil, especially an aviation turbine oil, is usually a minor proportion, preferably 0.001 to 10.0% by

weight, e.g. 0.01 to 5.0% by weight, based on the weight of lubricating oil.

The lubricating oil can be any mineral, animal, fish, vegetable or synthetic oil, for example, petroleum oil fractions ranging from spindle oil to SAE 30, 40 or 50 lubricating oil grades, castor oil, animal or fish oils or oxidised mineral oil, e.g. palm oil, lard oil, tallow oil, arachis oil or sperm oil.

The preferred lubricating oil is a synthetic ester and suitable diesters include diesters of the general formula

$ROOCR^1COOR$ and $RCOOR^1OOCR$

where R represents a C_6 to C_{12} alkyl group, while R_1 represents a C_4 to C_{10} saturated aliphatic hydrocarbon group or an ether-interrupted saturated aliphatic hydrocarbon group. The above types of esters may be prepared from alcohols and dicarboxylic acids or glycols and monocarboxylic acids.

Another suitable class of ester lubricant are the polyesters which are prepared by reacting polyhydric alcohols e.g. those having 2 to 12 hydroxyl groups per molecule and 2 to 40 carbon atoms per molecule, such as trimethylolpropane, pentaerythritol and dipentaerythritol with mono- and/or di-carboxylic acids such as butyric acid, caproic acid, caprylic acid and pelargonic acid, or adipic, sebacic or azelaic acids.

The complex esters which may be used as base oils are formed by esterification reactions between a dicarboxylic acid, a glycol and an alcohol and/or a monocarboxylic acid. These esters may be represented by the following formulae:

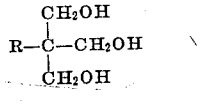
$R_4COO\text{-}R_3\text{—}(OOCR_2COO\text{—}R_3)_n\text{—}OOCR_4$

$R_1\text{—}OOCR_2COO\text{—}(R_3\text{—}OOCR_2COO)_n\text{—}R_1$

$R_1\text{—}(OOCR_2COO\text{—}R_3)_nOOCR_4$

wherein R_1 represents alkyl radicals derived from a monohydric alcohol, R_2 represents hydrocarbon radicals derived from a dicarboxylic acid, e.g. alkanedioic acids, R_3 represents divalent hydrocarbon or hydrocarbonoxy radicals such as $—CH_2(CH_2)_n—$, or $—CH_2CH\text{-}_2(OCH_2CH_2)_n—$, or $CH_2CH(CH_3)$ $(OCH_2CH(CH_3)\text{-})_n—$, derived from an alkylene glycol or polyalkyleneglycol, while R_4 represents the alkyl group derived from a monocarboxylic acid. n in the complex ester molecule which is an integer will usually range from 1 to 6 depending upon the product viscosity desired which is controlled by the relative molar ratio of the glycol or polyglycol to the dicarboxylic acid. In preparing the complex ester, there will always be some simple ester formed, i.e. n=0, but this will generally be a minor portion. In general these complex esters will have a total of between 15 and 80, e.g. between 20 and 65 carbon atoms per molecule.

Particularly suitable lubricants are esters of polyhydric alcohols having the formula



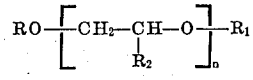
where R is a $—CH_2OH$ group or an alkyl group, e.g. an alkyl group containing 1 to 6 carbon atoms. Thus, suitable esters of this type are the neopentyl polyol esters of trimethylol ethane, trimethylol propane, trimethylol butane and of pentaerythritol or di-pentaerythritol.

The preferred acids used to esterify trimethylol propane are the C_4 to C_{12} monocarboxylic acids. Particularly preferred are the C_7–C_{10} esters, e.g. C_8 (caprylic) and C_9 (pelargonic) acid esters. Mixtures of these C_7–C_{12} acids may be used. When such an acid mixture is used, it is preferred that the mixture average between C_8 and C_9. Although more difficult to form, it is even more preferred that one methylol group be esterified with a neo-heptanoic acid, e.g. 2,2-dimethylpentanoic acid, and the remaining methylol groups esterified with non-hindered acids, e.g. pelargonic acid. This particular ester is substantially as thermally stable as the completely hindered ester but has superior volatility and low temperature characteristics.

The preferred acids used to esterify pentaerythritol are the C_4–C_{10} monocarboxylic acids with the more preferred esters being those of C_5 to C_9 acids, e.g. n-valeric, isovaleric, 2-ethyl butyric, caproic, n-heptylic, n-octanoic or 2-ethyl hexoic acids or a mixture of C_5 to C_9 acids.

Blends of diesters with minor proportions of one or more thickening agents may also be used as lubricants. Thus one may use blends containing up to 50% by volume of one or more water insoluble polyoxyalkylene glycols, for example, polyethylene or polypropylene glycol, or mixed oxyethylene/oxypropylene glycol.

Formulations suitable for gas turbine lubrication include from 65 to 90 vol.% of one or more diesters of azelaic or sebacic acid and a C_6–C_{16} branched chain alcohol, particularly of 2-ethyl hexanol, or "Oxo" alcohols consisting predominantly of C_8, C_9 or C_{10} alcohols, or of mixtures of such alcohols, and 35 to 10% of polyoxyalkylene glycol ether represented by the general formula:



wherein R_1, R and R_2 are hydrogen or C_1–C_{12} alkyl groups and wherein not more than two such groups is hydrogen, and n is an integer greater than 1. Particularly useful compounds are poly-oxypropylene glycol and mono-ethers and the corresponding diethers.

The thermal stability of such diester/polyoxyalkylene glycol ethers may be improved if a small proportion of a complex ester derived from three or more carboxylic acids or alcohols, at least two of which are difunctional acids or alcohols is incorporated. Such complex esters may be glycol- or dicarboxylic acid centered, the molecule being terminated with a mono-hydroxy or monocarboxylic acid compound. A particularly preferred complex ester of this type is derived from polyethylene glycol of molecular weight 200, 2 molecules of sebacic or azelaic acid, and 2 molecules of a C_6–C_{10} branched chain aliphatic monohydric alcohol, particularly 2-ethyl hexanol.

Other additives which may be incorporated in the lubricating oil include corrosion inhibitors, e.g. sebacic acid, a metal deactivator such as quinizarin, a foam inhibitor, e.g. a silicone polymer such as dimethyl silicone, an antioxidant, e.g. phenothiazine or dioctyl diphenylamine; or an antiwear additive, e.g. tricresylphosphate. Alternatively the mixture of amine salts can be added to a liquid fuel oil, e.g. a diesel fuel oil.

EXAMPLE 1

Tetrabutyl ammonium salts of mixtures of (1) methyl dihydrogen phosphate and di-methyl hydrogen phosphate (2) ethyl dihydrogen phosphate and di-ethyl hydrogen phosphate, and (3) n-butyl dihydrogen phos-

phate and di-n-butyl hydrogen phosphate were prepared according to the following procedure.

A 10% aqueous solution of the acid phosphate was stirred and tetra-n-butyl ammonium hydroxide solution (40% aq.) was added to adjust the pH to 7. The solution was evaporated to dryness in the presence of a trace of n-octanol to inhibit foaming. Toluene was added and the solution again evaporated to dryness: this was repeated once to ensure an anhydrous product.

For comparison purposes tetrabutyl ammonium salts of mixtures of C_6, C_8 and C_{12} n-alkyl dihydrogen and di-n-alkyl hydrogen phosphates were also prepared.

Each mixture was separately added to a synthetic ester base oil which also contained 1.0% by weight of tricresyl phosphate, 1.6% by weight of dioctyl diphenyl amine, and 0.4% by weight of phenothiazine. The base oil was a mixture of esters obtained by the esterification of 90% by weight pentaerythritol and 10% by weight dipentaerythritol with a mixture of (C_5–C_9) fatty acids.

The IAE gear machine failure load at 110°C/2000 RPM and the Rolls Royce Silicone Elastomer zero swell temperature (°C) were determined. The standard Rolls Royce silicone elastomer compatibility test (Method 1,009) involves the immersion of a standard test specimen in 50 ml. of test lubricant at a temperature of 175°C for 192 hours. High load carrying oils invariably cannot be made compatible with elastomers under these conditions and so in a modification of this method a series of tests were carried out at different temperatures and a plot of percent elastomer swell versus temperature was made. The temperature (extrapolated) at which the zero swell occurs is given as an index of elastomer compatibility of the oil. The results were as given in the following table. It can be seen that the best results as regards E.P. properties are obtained when tetrabutyl ammonium salts of the di-methyl hydrogen and methyl di hydrogen phosphates are used, and that the E.P. properties fall rapidly as the chain length of the groups R^5 and R^6 in the phosphate increases.

TABLE

Carbon Chain Length in acid phosphate mixture	Concentration wt.% P	wt.% (amine salt)	IAE gear machine Failure Load 2000 rpm/110°C. lb.	R-R Silicone Elastomer Zero Swell Temp. (°C)
12	10^{-2}	0.23	50	135
8	10^{-2}	0.20	60	132
6	10^{-2}	0.19	65	125
4	10^{-2}	0.17	63	—
2	10^{-2}	0.15	73	120
1	7×10^{-3}	0.10	108	125
1	5×10^{-3}	0.07	90	130

EXAMPLE 2

Hexyl trioctyl ammonium salts of mixtures of methyl dihydrogen phosphate and dimethyl hydrogen phosphate were prepared by the same procedure of Example 1 except that hexyl trioctyl ammonium hydroxide solution (40% aq.) was used instead of tetra-n-butyl ammonium hydroxide.

0.125% by weight (based on the weight of lubricating oil) of the mixed hexyl trioctyl ammonium salts was added to the same base oil as used in Example 1 which also contained the same quantities of tricresyl phosphate, dioctyl diphenyl amine and phenothiazine.

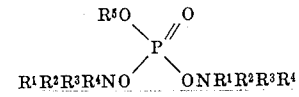
When subjected to the IAE gear machine and Rolls Royce Silicone Elastomer tests the following results were obtained.

IAE gear machine failure load 2000 rpm/110°C — 9.5lb.

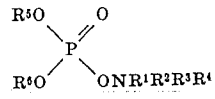
Rolls Royce Silicone Elastomer Zero Swell — 125°C.

What is claimed is:

1. A lubricating oil composition comprising a lubricating oil to which has been added from 0.001 to 10 percent by weight, based on the lubricating oil, of a mixture of about equal molar proportions of (a) a quaternary hydrocarbyl ammonium salt of mono (C_1–C_4) alkyl dihydrogen phosphate of the formula



and (b) a quaternary hydrocarbyl ammonium salt of di-(C_1–C_4) alkyl hydrogen phosphate of the formula



where R^1, R^2, R^3 and R^4 are similar or dissimilar hydrocarbon groups, R^1, R^2, R^3 and R^4 containing a total of at least 10 carbon atoms, and R^5 and R^6 similar or dissimilar are C_1–C_4 alkyl groups, said lubricating oil consisting essentially of polyester of a polyhydric alcohol selected from the class consisting of pentaerythritol, dipentaerythritol and mixtures of pentaerythritol and dipentaerythritol with a monocarboxylic acid or mixed monocarboxylic acids of from 4 to 10 carbon atoms.

2. A composition according to claim **1** wherein the total number of carbon atoms in R^1, R^2, R^3 and R^4 is at least 14.

3. A composition according to claim **2** wherein at least two of the groups R^1, R^2, R^3 and R^4 are the same.

4. A composition according to claim **1** wherein R^1, R^2, R^3 and R^4 are all n-butyl groups.

5. A composition according to claim **1** wherein R^5 and R^6 are both the same.

6. A composition according to claim **5** wherein R^5 and R^6 are both methyl groups or both ethyl groups.

7. A composition according to claim **1** which contains a mixture of hexyl trioctyl ammonium salts of methyl dihydrogen phosphate and dimethyl hydrogen phosphate.

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