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ESTER LUBRICANTS

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U.S. Cl. 252—46.6 5 Claims

ABSTRACT OF THE DISCLOSURE

Lubricating oil compositions having excellent anticorrosion and antioxidant properties consist of a major amount of an ester base lubricating oil and minor amounts each of a triaryl phosphorothionate and triaryl phosphate.

The present invention relates to ester lubricants. More particularly this invention relates to ester lubricants containing a mixture of phosphorus ester additives. Lubricants which are suitable for the lubrication of aviation gas turbines should possess a good oxidation stability at high temperatures and good extreme pressure properties. Such lubricants normally contain antioxidants, such as certain substituted phenothiazines and certain secondary aromatic amines and certain extreme pressure additives, such as triaryl esters of phosphorothionic acid.

Although these triaryl phosphorothionates have useful extreme pressure properties in ester lubricants, they cause corrosion of certain metals, in particular magnesium, cadmium and S.82 steel. This steel is an aircraft gear quality steel meeting British Standards Specification EN 39B.

Triaryl phosphates are well known extreme pressure additives, but ester lubricants containing them are deficient in high temperature oxidation stability.

It has now been found that triaryl phosphorothionates and triaryl phosphates work together in ester lubricants with respect to anticorrosion properties and antioxidant properties at high temperatures.

According to the present invention an ester lubricant comprises a major proportion of an ester lubricating oil and minor proportions each of a triaryl phosphorothionate and a triaryl phosphate.

The triaryl phosphorothionates useful in this invention contain 6 to 10 carbon atoms in each aryl group. The aryl groups in each triaryl phosphorothionate may be the same or different. Examples of suitable triaryl phosphorothionates include triphenyl-, tritolyl-, tribenzyl-, trixylyl- and diphenyltolyl-phosphorothionate. The preferred phosphorothionate is triphenyl phosphorothionate (TPPT).

The triaryl phosphates useful in this invention also contain 6 to 10 carbon atoms in each aryl group which may be the same or different. Suitable phosphates include triphenyl-, tritolyl-, tribenzyl-, trixylyl- and diphenyltolyl-phosphate. The preferred phosphate is triphenyl phosphate (TPP).

The ratio of triaryl phosphate to triaryl phosphorothionate in the lubricant may vary from 0.25:1 to 1:1, preferably the ratio will not be less than 0.5:1. The combined triaryl phosphates and triaryl phosphorothionates are present in an amount sufficient to provide anticorrosion and antioxidant properties. In general they will be present in an amount of 0.05 to 10% by weight and preferably from 0.1 to 5% by weight of the final composition.

Esters suitable as base oils in the present lubricant are simple esters, complex esters, polyesters, or mixtures

thereof. Thickeners may be added depending upon the viscometric properties desired for the composition and the temperature conditions under which it is to be used. By simple ester is meant an ester formed between an aliphatic dicarboxylic acid and aliphatic monohydric alcohol, preferred simple esters being formed from an aliphatic dicarboxylic acid containing from 6 to 10 carbon atoms in the molecule and a branched chain monohydric alcohol containing from 6 to 12 carbon atoms in the molecule, especially those alcohols having no hydrogen on the beta carbon atom. Examples of simple esters useful for the purposes of the present invention are diisononyl sebacate, di(2-ethylhexyl) sebacate, diisooctyl azelate, diisodecyl azelate, di(3,5,5-trimethyl hexyl) adipate, 2-ethyl hexyl-3,5,5-trimethyl hexyl sebacate and such simple hindered esters as 2,2,4-trimethyl pentyl azelate.

By complex ester is meant an ester formed from various combinations of an aliphatic dicarboxylic acid, a glycol or polyglycol and either or both of an aliphatic monohydric alcohol and an aliphatic monocarboxylic acid. Some typical complex ester structures are represented by AD(GD)nA, A(DG)nM and MG(DG)nM, wherein A, D, G and M represent the esterification residues from an aliphatic monohydric alcohol, an aliphatic dicarboxylic acid, a glycol or polyglycol and an aliphatic monocarboxylic acid respectively and n is a number from 1 to 6. Examples of typical starting materials suitable for the preparation of such esters are 2-ethyl butyl alcohol, 2-ethyl hexyl alcohol, caproic acids, pelargonic acid, capric acid, tertiary acids (non-α-hydrogen acids), neopentyl glycol, ethylene glycol, propylene glycol, polyglycols such as polyethylene glycols, sebacic acid, adipic acid, azelaic acid and pimelic acid.

By polyesters is meant esters made from aliphatic alcohols having therein at least 3 hydroxyl groups, for example esters made from trimethylol propane, e.g. trimethylol propane tripelargonate. Tetra esters such as the pentaerythritol tetra-esters or the dimers or trimers of the same and dipentaerythritol esters of C_4–C_{18} fatty acids, especially C_6–C_{14} fatty acids are preferred. These esters are commercially available from Hercules Chemical Company.

Thickeners may also be added to the oils of the invention to improve viscosity properties. As thickeners there may be used polymers of esters of acrylic or an alkyl-substituted acrylic acid, for example, lauryl methacrylate, or an ether of a polyoxyalkylene glycol of the general formula $R_5O(R_7O)_nR_6$, wherein R_5 is an alkyl group, R_6 is hydrogen or an alkyl group, R_7 is an alkylene group of 2 to 4 carbon atoms and n is a number greater than unity. Suitable compounds are marketed under the trade name "Ucon," specific examples being "LB385," "LB525," "LB625." Also suitable are copolymers of propylene oxide and ethylene oxide marketed under the trade name "Oxilube," e.g. Oxilube 85/140. The thickeners may be used in proportions of up to 50% by weight calculated on the final lubricant composition depending upon the viscometric properties required for said lubricant.

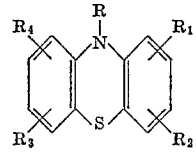
The ester lubricants of the present invention may also contain extreme pressure additives, antioxidants, metal deactivators, anticorrosion agents, antifoaming agents, dye stuffs and other additives know to be useful in ester base lubricant formulations.

Suitable additional extreme pressure additives which may be used in the invention are the clorinated di- or polyphenyls, i.e. diphenyls, terphenyls, higher polyphenyls or mixtures thereof containing at least one chlorine atom attached directly to each benzene nucleus, for example chlorinated di- or polyphenyls sold under the trade name "Arochlor." Particularly useful as E.P. additives are the monochloromethyl phosphonic acid

salts of tertiary alkyl primary amines, for example the monochloromethyl phosphonic acid salts of C_{18-22} tertiary alkyl primary amines.

Suitable as antioxidants are the substituted phenothiazines, secondary aromatic amines, alkylated phenols and bisphenols.

Particularly suitable as an anti-oxidant is a substituted phenothiazine having the formula:



where R is an alkyl, aryl, alkaryl, aralkyl or cyanoalkyl radical and at least one of R_1, R_2, R_3 and R_4 is an alkyl or alkoxy radical, any other being hydrogen and a secondary aromatic amine having two aromatic groups directly attached to the nitrogen atom. Especially useful are the combination 10-benzyl-3,7-dioctyl phenothiazine and phenyl-alpha-naphthylamine as taught in U.S. Patent 3,344,068.

A wide variety of material may be used as metal deactivators and anticorrosion agents, depending on the metal or metals with which the ester base composition of the present invention will come into contact. Materials which are particularly useful as affording protection of, for example, copper, copper alloys and silver against corrosive attack are the triazoles, for example 1,2,3-benztriazole, methyl - 1,2,3 - benztriazole, 3-amino-5-methyl-1,2,4-triazole, especially 3-amino - 5-phenyl-1,2,4-triazole, 3-amino-5-pyridyl - 1,2,4- triazole, 3-amino 5-anilido - 1,2,4-triazole and 5,5'-diamino - 3,3-bi (1,2,4,-triazole) used in amounts up to about 1%, preferably about 0.5% by weight of the composition. Also useful for providing protection for metals such as copper, cadmium, silver and magnesium are minor amounts, e.g. up to 1% by weight, preferably up to 0.5% by weight of pyridylamines, particularly dipyridylamines, e.g. 2,2'-dipyridylamine. Small proportions, e.g. from 0.01 to 0.2% by weight, of sebacic, azelaic or adipic acid are useful as inhibitors of lead corrosion while metal petroleum sulfonates, e.g., calcium petroleum sulfonate are useful as rust inhibitors.

Suitable antifoaming agents are the polydimethyl siloxanes having viscosities from 100 to 100,000 centistokes at 25° C.

To illustrate the effectiveness of the compositions of the present invention the compositions shown in Table I were prepared. Compositions A–E are not in accordance with the present invention and are included for comparative purposes. Compositions F–J were formulated according to the invention.

TABLE 1

Composition, Percent Weight	A	B	C	D	E	F	G	H	J
Hercolube A [a]	64.5	64.5	64.5	64.5	64.5	64.5	64.5	64.5	64.5
Hercolube F [b]	31.9	31.9	31.9	31.9	31.9	31.9	31.9	31.9	31.9
N-benzyl-3,7-dioctylphenothiazine	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Phenyl-alphanaphthylamine	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Azelaic acid	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Silicone fluid MS 200/12500	[c] 5	[c] 5	[c] 5	[c] 5	[c] 5	[c] 5	[c] 5	[c] 5	[c] 5
JMT/MCMPA [d]	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17
3-amino-5-phenyl-1,2,4-triazole	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Triphenylphosphorothionate		0.5			1.0	1.0	1.0	0.5	1.0
Triphenylphosphate			0.5	1.0		0.5	1.0	0.5	0.3

[a] Pentaerythritol esters of saturated fatty acids.
[b] Dipentaerythritol esters of saturated fatty acids.
[c] Parts per million.
[d] C_{18-22} tertiary alkyl primary amine salts of monochloromethyl phosphonic acid.

The following tests were carried out on the above compositions and the results are given below in Tables 2-6.

Bristol siddeley corrosion test

This test involves exposing certain specimens to the ester composition to be tested for a period of 24 hours as a temperature of 285° C. Changes in weight of the metal specimens are determined. The results are recorded in Table 2.

TABLE 2

Composition	Weight Change, mg./sq. cm.										
	Brass	Monel	Aluminium	Bronze	S.82 Steel	Cast Iron	Silver	S110B [a] Steel	Cadmium	Magnesium	Nickel
B	−2.0	Nil	Nil	−0.14	−19	−2.7	Nil	−0.24	−11	>−130	Nil
C	−0.56	Nil	+0.04	Nil	−0.19	−0.64	−0.06	+0.07	−2.7	−28	+0.04
D	−0.74	Nil	Nil	Nil	−0.17	−0.46	+0.04	Nil	−0.69	−29.8	−0.06
E	−0.70	+0.10	−0.03	−0.2	−21.0	−4.03	+0.01	−1.59	−49.0	>−130	+0.03
F	−0.13	Nil	Nil	−0.07	−0.37	Nil	Nil	Nil	−3.9	−12	+0.08
G	+0.01	Nil	Nil	Nil	Nil	Nil	Nil	Nil	−2.90	−11.1	+0.07
H	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	−3.20	−10.4	Nil
J	−0.51	Nil	Nil	−0.13	−5.1	−0.81	Nil	−0.04	−0.51	−100	+0.10

[a] S110B Steel is a corrosion resistant welding quality stainless steel meeting British Standards Spec. En58C.

From Table 2 it is obvious that the ester oil composition containing the combination of triphenyl phosphorothionate and triphenyl phosphate is significantly less corrosive than the oil composition containing triphenyl phosphorothionate alone. This is particularly evident in regards to magnesium, cadmium and S.82 steel. Although the magnesium result for Composition J is disappointing the results for Compositions F, G and H show that increasing the ratio of triphenyl phosphate to triphenyl phosphorothionate does give considerably improved results.

Rolls-Royce blown oxidation test

This test comprises bubbling air saturated with water vapor, at a fixed rate, through 50 ml. of the ester composition to be tested for a period of 24 hours at 250° C. Deterioration of the composition due to oxidation is then measured in time of viscosity change as shown in Table 3. The results shown are for duplicate runs.

TABLE 3

	Percent Increase in Viscosity at 100° F.
Composition:	
D	663; 548
E	320; 298
G	155; 159
H	343; 346

From Table 3 it is clear that there is a high temperature co-antioxidant effect between triphenyl phosphorothionate and triphenyl phosphate.

Rolls-Royce corrosion test method 1002

The above corrosion test determines weight changes of selected metals suspended in test compositions at a temperature of 200° C. for 192 hours.

Prior to the test the test compositions are pretreated by heating about 100 mls. of the composition in a stainless steel container with a close fitting cap fitted with a narrow steel condenser for 5 hours at 325° C.

The results of the above test are given in Table 4.

TABLE 4

	Metal Weight Change, mg./sq. cm.									
Composition	Al	Ti/Cu	Cu/Ni/Si	Mild Steel	Pb Bronze	High C/Cr Steel	Pb Brass	Ni/Cr Case Hardened Steel	High Speed Steel	Cu
D	Nil	Nil	−1.2	−8.9	−1.2	−3.7	−2.1	−0.27	−0.03	−1.5
E	Nil	Nil	−1.8	−36	−4.3	−16	−6.4	−21	−6.3	−2.0
G	Nil	Nil	−0.94	−6.1	−0.86	−2.9	−1.8	−2.6	−0.23	−1.5

The results of Table 4 indicate that the corrosivity resulting from the use of triphenyl phosphorothionate at high temperatures is greatly diminished when triphenyl phosphate is added to the composition.

A danger of using triphenyl phosphate in an ester lubricant is that a phosphate can be hydrolysed to an acid phosphate which can then catalyze the partial hydrolytic degradation of the ester to its half ester which is corrosive. Moreover the alcohol which is formed lowers the flash-point. The hydrolytic tendency of the composition of this invention has been examined by means of two well-known and accepted tests, namely, the Rolls-Royce Hydrolytic Stability Test and the S.O.D. Lead Corrosion/Storage Stability Test.

The Rolls-Royce Hydrolytic Stability Test involves heating 250 mls. of a composition with 25 mls. distilled water at 90° C. until the acidity value increases by 1.5 mgms. KOH/gm. In the S.O.D. Test a lead test piece and a copper catalyst piece are mounted on a stirrer immersed in the composition under test and rotated at a specific speed. Air is bubbled through the composition, maintained at 325° F., at a specified flow rate for 1 hour. The above is carried out on a new composition and after the composition has been stored for 7 days at 230° F.

Table 5 gives the results of these two tests.

TABLE 5

	Composition		
Test	D	E	G
R.R. Hydrolytic Stability Test: Time in hours for acidity value to increase by 1.5 mg. KOH/gm.	134	124	126
S.O.D. Test:			
Lead weight loss after 1 hr. at 325° F. mg./sq. inch:			
New composition	−0.19	−0.67	Nil
After storage 7 days at 230° F	−1.86	−0.56	−0.49

The above results indicate that the triphenyl phosphate does not have a deleterious hydrolytic effect on the ester base.

Finally the action of triphenyl phosphate (TPP) on conventional esters such as di-isooctyl azelate was noted. The results in Table 6 show that a di-isooctyl azelate formulation containing 1% triphenyl phosphate but no triphenyl phosphorothionate (TPPT) does exhibit higher lead corrosion (i.e. greater hydrolysis) than the same ester having 1% TPP and 1% TPPT.

TABLE 6

	Composition	
S.O.D. test	Ester plus 1% TPP	Ester plus 1% TPP plus 1% TPPT
Lead weight loss at 325° F. for 1 hour after storage for 7 days at 230° F, mg./sq. inch	5.45	0.19

We claim as our invention:

1. A lubricating composition containing a major amount of a carboxylic ester base lubricating oil and a minor amount, sufficient to inhibit corrosion and provide high temperature stability to the oil, each of a triaryl phosphorothionate and a triaryl phosphate in which each aryl group of the phosphorothionate and of the phosphate compounds contains 6–10 carbon atoms.

2. The composition of claim 1 wherein the triaryl phosphorothionate and triaryl phosphate comprise about 0.05 to 10% by weight of the lubricating composition.

3. The composition of claim 2 wherein the ratio of triaryl phosphate to triaryl phosphorothionate varies from 0.25:1 to 1:1.

4. The composition of claim 3 wherein the triaryl phosphorothionate is triphenyl phosphorothionate and the triaryl phosphate is triphenyl phosphate.

5. The composition of claim 4 wherein the ester base lubricating oil is a mixture of saturated fatty acid esters of pentaerythritol.

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