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3,344,068

ESTER BASE LUBRICANTS

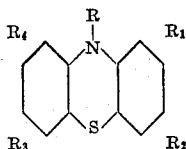
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This application is a continuation-in-part of application Ser. No. 436,945, filed Mar. 3, 1965 (now abandoned).

This invention relates to an ester base lubricant having good oxidation stability which is particularly useful for lubricating gas turbine engines.

Oils of the invention comprise major amounts of an ester base oil and minor amounts sufficient to enhance the oxidation stability of

(1) An N-substituted phenothiazine having the formula



wherein R is selected from a hydrocarbyl group having 1 to 12 carbons, preferably 1 to 6 carbons, and a cyanoalkyl group having 1 to 20 carbons, preferably 2 to 8 carbons; R₁ is selected from the group consisting of alkyl and alkoxy groups having from 1 to 12, preferably 4 to 8, carbons; and R₂, R₃, and R₄ are selected from the group consisting of hydrogen and C₁-C₁₂, preferably C₄ to C₈, alkyl and alkoxy groups; and

(2) A secondary aromatic amine having two aromatic groups attached to the nitrogen atom.

The hydrocarbyl group can be alkyl, aryl, alkaryl, or aralkyl.

The N-substituted phenothiazines of the present invention preferably have one alkyl or alkoxy radical as substituent in each aromatic ring comprising the phenothiazine molecule and 3,7-substitution is most preferred. Preparation of N-substituted phenothiazines is described, for example, in British Patent No. 873,066, issued July 19, 1961, to Shimmin and Moffatt. N-substituted phenothiazines which are particularly useful for the purposes of the present invention are 10-methyl-3,7-dioctyl phenothiazine, 10-n-butyl-3,7-dioctyl phenothiazine, 10-n-octyl-3,7-dioctyl phenothiazine, 10-phenyl-3,7-dioctyl phenothiazine, 10-tolyl-3,7-dioctyl phenothiazine, 10-cyanoethyl-3,7-dioctyl phenothiazine, 10-cyanopropyl-3,7-dioctyl phenothiazine, 10-cyanobutyl-3,7-dioctyl phenothiazine, 10-benzyl-3,7-dioctyl phenothiazine, 10-benzyl-3,7-dibutyl phenothiazine, 10-benzyl-3,7-diisopropoxy phenothiazine, 10-benzyl-3,7-dibutoxy phenothiazine and mixtures thereof.

Any secondary aromatic amine may be used in conjunction with the N-substituted phenothiazines for the purposes of the present invention; certain diphenylamines and N-aryl naphthylamines are, however, preferred. Suitable diphenylamines are unsubstituted diphenylamine and those having an alkyl or alkoxy radical containing from 4 to 20 carbon atoms substituted in the para position of at least one aromatic nucleus; di-substituted diphenylamines are preferred, particularly p,p'-dioctyl diphenylamine. Examples of N-aryl naphthylamines, which may be alkyl substituted in at least one aromatic nucleus by one or more alkyl groups which may contain a total of up to 20 carbon atoms, include phenyl- α -naphthylamine, phenyl- β -naphthylamine and β,β -dinaphthylamine; phenyl-

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α -naphthylamine is preferred. It also appears that when the ester comprising the major proportion of the present ester base composition is a simple ester it is preferable to use diphenylamines, e.g., p,p'-dioctyldiphenylamine, especially in admixture with N-aryl naphthylamines, as the secondary aromatic amine, whereas N-aryl naphthylamines, e.g. phenyl- α -naphthylamine, appear to be preferable for use with polyesters.

The additives of the invention are employed in minor amounts sufficient to enhance the oxidation stability of the oil; in general, they will be present in an amount of 0.05 to 10% by weight, preferably 0.1 to 5% by weight of the final composition.

Esters suitable as the ester base in the composition of the present invention are simple esters, complex esters, polyesters, or mixtures thereof to which may be added other additives, depending upon the 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 an 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 diisooctyl sebacate, di(2-ethyl hexyl) sebacate, diisooctyl azelate, di(3,5,5-trimethyl hexyl) adipate, 2-ethyl hexyl-3,5,5-trimethyl hexyl sebacate and 2,2,4-trimethyl pentyl azelate.

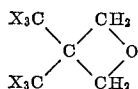
By complex ester is meant an ester formed from various combinations of an aliphatic dicarboxylic acid, a glycol or polyglycol and either or both of an aliphatic monohydric alcohol and an aliphatic monocarboxylic acid. Some typical complex ester structures are represented by AD(GD)*n*A, A(DG)*n*M and MG(DG)*n*M, 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 material suitable for the preparation of such esters are 2-ethyl butyl alcohol, 2-ethyl hexyl alcohol, caproic acids, pelargonic acid, capric acid, neopentyl glycol, ethylene glycol, propylene glycol, polyglycols such as polyethylene glycols, sebacic acid, adipic acid, azelaic acid and pimelic acid.

By polyesters in meant esters made from aliphatic alcohols having therein at least 3 hydroxyl groups, for example esters made from trimethylol propane. Tetraesters such as pentaerythritol tetraesters of dimers or trimers of the same and dipentaerythritol esters of C₄-C₂₀ acids, especially C₅-C₁₀ acids, are particularly preferred. These esters are commercially available from Hercules Chemical Company.

Thickeners may also be added to oils of the invention to improve viscosity properties. Suitable thickeners are 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 R₅O(R₇O)*n*R₆, wherein R₅ is an alkyl group, R₆ is hydrogen or an alkyl group, R₇ 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 "Uncon," 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 40% by weight calculated on the final lubricant composition depending upon the viscometric properties required for said lubricant.

The ester base compositions of the present invention may additionally contain extreme pressure additives, additional antioxidants, metal deactivators, anti-corrosion agents, anti-foaming agents, dyestuffs, and other additives known to be suitable for use with ester base lubricant formulations.

Suitable E.P. agents are esters of acids of phosphorus, such as triphenyl phosphorothionate, tritoyl phosphorothionate, and trixylyl phosphorothionate; phosphate esters e.g. triphenyl phosphate and tritoyl phosphate may also be used but are preferably used in conjunction with a minor proportion e.g. 0.1% weight based on the whole lubricant formulation of a secondary amine such as dimethyl (3,5-ditertiary butyl-4-hydroxy benzyl)amine. Another class of phosphorus-containing E.P. additives which may be employed in ester base compositions of the present invention are diaryl haloalkyl phosphates, e.g. diphenyl-2,2-bis(chloromethyl)3-chloromethyl phosphorothionate. Yet another class of E.P. additives which may usefully be employed in the present ester base compositions are the chlorinated 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." Still another class of E.P. additives suitable for use in ester base compositions of the present invention are substituted oxetane polymers, i.e. polymers prepared from oxetanes having the formula



wherein one X is chlorine or bromine and the others are chosen from hydrogen, chlorine or bromine, e.g. 3,3-bis(chloromethyl)oxetane.

A class of E.P. additives which are particularly useful for imparting extra resistance to extreme pressure conditions are the monochloromethylphosphonic acid salts of tertiary alkyl primary amines, for example the mono-

chloromethylphosphonic acid salts of C₁₈₋₂₂ tertiary alkyl primary amines.

A wide variety of materials may be used as metal deactivators and anti-corrosion 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-benzotriazole, methyl-1,2,3-benzotriazole, 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% wt. 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 anti-foaming agents are the polydimethyl siloxanes having viscosities from 100 to 100,000 centistokes at 25° C.

To illustrate the ester base compositions of the present invention, compositions as shown in Table I (Examples I-III and VII-VIII) were formulated and thereafter compared with corresponding compositions (Examples IV-VI and IX-X) not in accordance with the present invention by means of one or more of three test procedures, viz. the oxidation/corrosion test at 175° C. set forth in U.S. Military Specification MIL-L 7808D, a low-temperature storage test and an accelerated storage test. In the storage tests samples of compositions in accordance with the present invention and comparative examples not in accordance with the present invention were stored in containers having loosely fitting lids, maintained at temperatures of 15° C. and 80° C. and examined periodically after periods up to three months for the presence of suspended matter.

TABLE I

Composition of Examples I-X	I	II	III	IV	V	VI	VII	VIII	IX	X
Di(2-ethyl hexyl)sebacate, percent wt.		94.0			94					
Dihsoctyl azelate, percent wt.	93.2			93.2			93.2	30.2	93.2	30.2
Disododecyl azelate, percent wt.								34.0		34.0
2,2,4-trimethyl pentyl azelate, percent wt.			14.5							
Trimethylol propane tripelargonate, percent wt.			58.0				14.5			
Hercolube "A", ¹ percent wt.			19.5				58.0			
Oxilube ² 85/140, percent wt.							19.5			
10-benzyl-3,7-dioctyl phenothiazine, percent wt.								33		33
3,7-dioctyl phenothiazine, percent wt.	1.5	1.5	1.5				1.3	1.3		
Phenyl- α -naphthylamine, percent wt.				1.5	1.5	1.5			1.3	1.3
Aroclor ³ 1254, percent wt.	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Triphenyl phosphorothionate, percent wt.	3.0		3.0	3.0			3.0		3.0	
5-methyl benzotriazole, p.p.m.	1.0		2.0	1.0			2.0		1.0	
3-amino-5-anilido-1,2,4-triazole, p.p.m.		25	25		25	25				
Azelaic acid, percent wt.	25			25			25	25	25	25
Silicone MS 200/12500, p.p.m.	0.02	0.02	0.02	0.02	0.02	0.02	0.02		0.02	
Polymer of 3,3'-bis(chloromethyl) oxetane (molecular weight 450, Cl content 45%), percent wt.	5	5	5	5	5	5	5		5	
		3			3					

¹ C₇-C₁₀ acid esters of pentaerythritol.

² Copolymers of ethylene oxide and propylene oxide.

³ Chlorinated diphenyl.

TABLE II

Example No.	Volatility Loss, Percent wt.	Acidity Increase, mg. KOH/g.	Viscosity Increase, Percent	Metal Weight Change, mg./cm. ²				
				Cu	Mg	Ag	Al	Fe
I	0.8	1.25	12.0	Nil	Nil	Nil	Nil	Nil
II	0.6	1.5	12.2	-0.10	Nil	0.12	Nil	Nil
III	0.4	0.5	2.6	-0.03	Nil	+0.02	Nil	-0.02
IV	0.7	1.20	11.8	-0.04	Nil	Nil	Nil	Nil
V	1.2	1.5	12.6	Nil	+0.12	-0.3	Nil	-0.02
VI	0.4	0.4	2.5	-0.02	+0.02	Nil	Nil	Nil
Specification Limits		2.0	-5 to +15	±0.4	±0.2	±0.2	±0.2	±0.2

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From Table II it is clear that the formulations of Examples I-III (i.e. formulations according to the invention) all show a resistance to oxidation and corrosion at high temperature which is at least as good as that shown by the comparative formulations IV-VI (i.e. formulations outside of the invention) while the formulation of Example I has exceptional high-temperature oxidation and corrosion resistance. Referring now to Table III it is clear that only the formulations of Examples I-III and VII-VIII (i.e. formulations according to the present invention) give satisfactory performance in the storage tests. Four samples of each of the formulations of Examples VII-X were also subjected to low-temperature (15° C.) storage for a period of a year and were examined for suspended matter at intervals of a few weeks. All of the samples of Examples VII and VIII so stored (i.e. samples of compositions of the invention) remained clear and bright throughout the entire low-temperature test period, whereas the behavior of samples of the comparative Examples IX and X was variable, one sample of each example remaining clear, some samples of each example giving deposition in the first few days of storage, while all of the remaining samples gave deposition before the end of the test period.

TABLE III

Example No.	Condition of Sample after—					
	15° C.	80° C.				
	3 months	3 weeks	5 weeks	7 weeks	8 weeks	12 weeks
I.....	Clear.....				Clear.....	
II.....	do.....				do.....	
III.....	do.....				do.....	
IV.....	Cloudy.....				Cloudy.....	
V.....	do.....				White ppt.....	
VI.....	do.....				Cloudy.....	
VII.....		Clear.....	Clear.....	Clear.....		Clear.....
VIII.....		do.....	do.....	do.....		Do.....
IX.....		do.....	Cloudy.....	Deposition.....		Medium deposition.....
X.....		Cloudy.....	Deposition.....	Medium deposition.....		Heavy deposition.....

To illustrate the advantage to be gained from employing a diphenylamine, particularly when admixed with an N-aryl naphthylamine, in conjunction with the N-substituted phenothiazine, when the ester comprising the major proportion of the ester base composition of the present invention is a simple ester, the compositions referred to as Examples XI, XII and XIII in Table IV were tested by means of the Rolls Royce Blown Oxidation Test. In this test, 250 ml. per minute of air or nitrogen, saturated with water vapor, are bubbled under controlled conditions through a 50-ml. sample of the ester base composition under test at a temperature of 198° C. for a period of 192 hours. Deterioration of the composition due to oxidation is then measured in terms of acidity, viscosity change and benzene insolubles.

TABLE IV

Example/Composition, percent wt.	XI	XII	XIII
Diisooctylazolate.....	94.0	93.5	96.0
10-benzyl-3,7-dioctyl phenothiazine.....	0.5	0.5	0.5
Phenyl- α -naphthylamine.....	0.5		0.5
p,p'-Dioctyldiphenylamine.....	2.0	2.0	
Azelaic acid.....	0.02	0.02	0.02
Aroclor 1254.....	3.0	3.0	3.0
3-amino-5-anilido-1,2,4-triazole (p.p.m.).....	25	25	25
Silicone MS 200/12500 (p.p.m.).....	5	5	5

The results obtained are appended at Table V, from which it is seen that the composition of Example XI, which comprised a simple ester and a mixture of secondary aromatic amines in conjunction with an N-substituted phenothiazine, gave less benzene insolubles, a smaller viscosity increase and a smaller acidity increase than did the composition of Example XII, which comprised a simple ester and a diphenylamine in conjunc-

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tion with an N-substituted phenothiazine, while Example XII gave less benzene insolubles, a small viscosity increase and a smaller acidity increase than did the composition of Example XIII, which comprised a simple ester and phenyl- α -naphthylamine in conjunction with an N-substituted phenothiazine.

TABLE V

Example No.	Benzene Insolubles, percent wt.	Viscosity at 210° F., cs., percent increase	Acid Value, mg. KOH/g.	
			Initial	Final
XI.....	0.01	10.0	0.10	3.6
XII.....	0.013	11.3	0.10	5.5
XIII.....	0.20	15.2	0.10	5.8

N-cyanoalkyl substituted phenothiazines suitable for the purposes of the present invention are those having up to 20, preferably from 2 to 8, carbon atoms in the alkyl chain of the cyano alkyl radical and preferably have one

alkyl or alkoxy radical on each aromatic ring comprising the phenothiazine molecule; 3,7-disubstitution is preferred. Examples of such phenothiazines are 10-cyanoethyl-3,7-dioctyl phenothiazine, 10-cyanopropyl-3,7-dioctyl phenothiazine, and 10-cyanobutyl-3,7-dioctyl phenothiazine.

As a further illustration of ester-based compositions of the present invention the compositions referred to as Examples XV and XVI in the accompanying Table VII were tested by means of the aforesaid Rolls Royce Blown Oxidation Test.

TABLE VII

Example/Composition, percent wt.	XV	XVI
Diisooctylazolate.....	93.0	93.0
10-cyanoethyl-3,7-dioctyl phenothiazine.....	1	
10-benzyl-3,7-dioctyl phenothiazine.....		1
p,p'-Dioctyldiphenylamine.....	2	2
Triphenylphosphorothionate.....	1	1
Aroclor 1254 (a chlorinated diphenyl).....	3	3
Azelaic acid.....	0.02	0.02
3-amino-5-phenyl-1,2,4-triazole (p.p.m.).....	25	25
Silicone MS 200/12500 (p.p.m.).....	5	5

The results obtained are set out at Table VIII from which it is seen that the composition of Example XV which comprises an N-cyanoalkyl substituted phenothiazine and a secondary aromatic amine gives a performance in the Rolls Royce Blown Oxidation Test which is at least as good as that given by the composition of Example XVI (a composition of the present invention) comprising 10-benzyl-3,7-dioctyl phenothiazine.

TABLE VIII

Example No.	Benzene Insolubles, percent wt.	Viscosity at 210° F., cs., percent increase	Increase in Acid Value, mg. KOH/g.
XV.....	0.02	9.5	4.3
XVI.....	0.01	9.5	6.3

The results obtained by submitting further compositions in accordance with the present invention to the Rolls Royce Blown Oxidation Test are set out at Table IX and are identified as Examples XVII to XXI. In these examples the formulation of Example XV was used except that the substituent on the nitrogen atom of the substituted phenothiazine was varied.

TABLE IX

Example No.	Substituent on Nitrogen Atom	Benzene Insolubles, percent wt.	Viscosity at 210° F., cs., percent increase	Increase in Acid Value, mg. KOH/g.
XVII.....	Tolyl.....	0.03	8	4.9
XVIII.....	Phenyl.....	0.03	8	3.8
XIX.....	Methyl.....	0.01	7	Nil
XX.....	n-Butyl.....	0.01	7	Nil
XXI.....	n-Octyl.....	0.01	7.5	0.02

A further example still (Example XXII) of a composition in accordance with the present invention is given at Table X.

TABLE X

Component	Percent wt.
Hercolube A (pentaerythryl ester of C _{6,5} acids) ..	64.0
Hercolube F (dipentaerythryl ester of C ₄₋₁₀ acids) ..	31.6
N-benzyl-3,7-dioctyl phenothiazine	1.7
Phenyl- α -naphthylamine	1.5
Triphenyl phosphorothionate	1.0
Primene JMT/MCMPA (a monochloromethyl phosphonic acid salt of a mixture of C ₁₈ -C ₂₂ tertiary alkyl primary amines)	0.2
3-amino-5-anilido-1,2,4-triazole	0.2
Azelaic acid	0.02
MS 200/12,500, 5 p.p.m.	

When subjected to the Rolls Royce Blown Oxidation Test carried out at a test temperature of 225° C., the formulation of Example XXII (Table X) gave only 0.01% weight benzene insolubles and an increase in acidity of 4.9 mg. KOH/g. Furthermore the composition gave no deposition after storage for twelve weeks at a tem-

perature of 80° C. and has highly desirable load-carrying properties, giving an I.A.E. gear rig scuffing load of 66 lbs. lever load under condition C of I.P. Method No. 166 and a Ryder gear rig scuffing load in excess of 3,300 lbs.

We claim as our invention:

1. A lubricating composition comprising a major amount of an ester base lubricating oil and minor amounts sufficient to increase the oxidation stability of the oil of

- (1) 10-benzyl-3,7-dioctylphenothiazine, and
- (2) a secondary aromatic amine having two aromatic groups attached to the nitrogen atom.

2. The composition of claim 1 wherein the secondary aromatic amine is a diphenylamine.

3. The composition of claim 1 wherein the secondary aromatic amine is a p,p'-disubstituted diphenylamine.

4. The composition of claim 1 wherein the secondary aromatic amine is a N-aryl naphthylamine.

5. The composition of claim 1 wherein the secondary aromatic amine is phenyl- α -naphthylamine.

6. A lubricating composition comprising a major amount of an ester base lubricating oil and about 0.1 to about 5% by weight of each of 10-benzyl-3,7-dioctylphenothiazine and phenyl- α -naphthylamine.

7. A lubricating composition comprising a major amount of an ester base lubricating oil and about 0.1 to about 5% by weight of each of 10-benzyl-3,7-dioctylphenothiazine and p,p'-dioctyl diphenylamine.

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