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3,843,531

SYNTHETIC AIRCRAFT TURBINE OIL

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11 Claims

ABSTRACT OF THE DISCLOSURE

Synthetic lubricating oil composition comprising a major portion of an aliphatic ester base oil having lubricating properties formed from the reaction of a pentaerythritol of trimethylolpropane and an organic monocarboxylic acid containing (a) from about 0.005 to 0.5 percent of a dihydrocarbylamine salt of axalic acid; (b) from about 0.3 to 5 percent of an alkyl or alkaryl phenyl-naphthylamine; (c) from about 0.3 to 5 percent of a dialkyldiphenylamine; and (d) from about 0.25 to 10 percent of a hydrocarbyl phosphate ester.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention is concerned with the lubricating oil composition used in a gas turbine or jet engine. Gas turbine engines are operated under extreme environmental conditions. The lubricant must be fluid at extremely low temperature and must be an effective lubricant in an engine which produces internal engine temperatures in the range of 450-500° F. or above. These operating conditions put severe stresses on the lubricating oil, so much so that the most advanced mineral lubricating oil compositions cannot be employed in gas turbine engines.

Currently, synthetic ester base lubricating oil compositions containing a critically balanced blend of additives are being effectively employed for lubricating gas turbine engines. These ester base oils are operative over a wide temperature range and exhibit high thermal stability, antiwear, load-carrying and anti-oxidation, properties while providing good lubrication.

With the advent of newer and more powerful gas turbine engines designed to provide advanced levels of supersonic flight, higher levels of thermal and oxidative stresses are imposed on the lubricating oil. It is also important to reduce or prevent staining and corrosion by the oil composition.

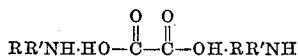
DESCRIPTION OF THE PRIOR ART

U.S. 3,427,111 discloses a synthetic lubricating oil composition employing a pentaerythritol ester base containing (1) arylamine type anti-oxidants, such as diphenylamine and phenyl-alpha naphthylamine, (2) a copper surface passivator, namely a salt of 1-salicylalaminoguanidine and a C₁₄₋₁₈ aliphatic carboxylic acid, (3) a metal deactivator, namely a polyhydroxyanthraquinone and (4) an organic phosphorus ester in the form of a phosphate or a phosphite.

SUMMARY OF THE INVENTION

The synthetic lubricating oil composition of the invention comprises a major portion of an aliphatic ester base oil having lubricating properties containing an amine salt of oxalic acid, an alkylphenyl or alkarylphenyl naphthylamine, a dialkyldiphenylamine, and a hydrocarbyl phosphate. More specifically, the lubricating oil composition of the invention comprises a major portion of an aliphatic ester base oil formed from the reaction of a pentaerythritol or trimethylolpropane and an organic monocarboxylic acid having from about 2 to 18 carbon atoms per molecule containing:

- (a) From about 0.005 to 0.5 weight percent of a dihydrocarbylamine salt of oxalic acid represented by the formula:



in which R is a hydrocarbyl radical having from about 8 to about 22 carbon atoms and R' is hydrogen or a hydrocarbyl radical having from about 1 to 5 carbon atoms.

- (b) From about 0.3 to 5 percent by weight of the lubricating oil composition of alkyl or alkaryl derivatives of phenyl α or β naphthylamines in which the alkyl radicals have from 4 to 12 carbon atoms,
- (c) From about 0.3 to 5 percent of a dialkyldiphenylamine in which the alkyl radicals have from 4 to 12 carbon atoms, and
- (d) From about 0.25 to 10 percent of a hydrocarbyl phosphate in which said hydrocarbyl radical contains an aryl ring and has from about 6 to 18 carbon atoms.

The lubricating oil of the invention provides outstanding thermal and oxidative stability and effectively reduces or prevents metal staining and corrosion. The realization of these valuable properties was most surprising and unexpected because of the unique nature of this synthetic ester base lubricating oil composition.

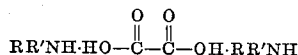
The base fluid component of the lubricant of the invention is an ester-base fluid prepared from pentaerythritol or trimethylolpropane and a mixture of hydrocarbyl monocarboxylic acids. Polypentaerythritols can also be employed in the reaction to prepare the base oil.

The hydrocarbon monocarboxylic acids which are used to form the ester-base fluid include the straight-chain and branched-chain aliphatic acids, cycloaliphatic acids and aromatic acids as well as mixtures of these acids. The acids employed have from about 2 to 18 carbon atoms per molecule, and preferably from about 5 to 10 carbon atoms. Examples of suitable specific acids are acetic, propionic, butyric, valeric, isovaleric, caproic, decanoic, hexadecanoic, vinylbenzoic, dodecylbenzoic, pelargonic, decanoic, cyclohexanoic, naphthenic, benzoic acid, phenylacetic, tertiarybutylacetic acid and 2-ethylhexanoic acid.

In general, the acids are reacted in proportions leading to a completely esterified pentaerythritol or trimethylolpropane with the preferred ester bases being the pentaerythritol tetraesters. Examples of such commercially available tetraesters include pentaerythritol tetracaprate, which is prepared from purified pentaerythritol and crude caproic acid containing other C₅₋₁₀ monobasic acids. Another suitable tetraester is prepared from a technical grade pentaerythritol and a mixture of acids comprising 38 percent valeric, 13 percent 2-methyl pentanoic, 32 percent octanoic and 17 percent pelargonic acids. Another effective ester is the triester of trimethylolpropane in which the trimethylolpropane is esterified with a monobasic acid mixture consisting of 2 percent valeric, 9 percent capronic, 13 percent heptanoic, 7 percent octanoic, 3 percent caprylic, 65 percent pelargonic and 1 percent capric acids. Trimethylolpropane triheptanoate, trimethylolpropane-entanoate and trimethylolpropanehexanoate are also suitable ester bases.

The ester base comprises the major portion of the fully formulated synthetic ester base lubricating oil composition. In general, this ester base fluid is present in concentration from about 90 to 98 percent of the composition.

The essential diamine or neutral salt of oxalic acid is represented by the formula:



in which each R is a hydrocarbyl radical having from about 8 to about 22 carbon atoms and R' is hydrogen or a hydrocarbyl radical having from about 1 to 5 carbon atoms. A preferred class of amine salts of oxalic acid are those in which R is an aliphatic radical and, more particularly, those in which R is a saturated aliphatic hydrocarbon radical having from about 12 to about 18 carbon atoms.

The method for preparing the prescribed amine salts of oxalic acid is well known. In general, two moles of a suitable amine are refluxed with a mole of oxalic acid dihydrate preferably in a mutual solvent, such as benzene and the like, and the water collected and measured in order to determine when the reaction is complete. The reaction mixture is then concentrated under reduced pressure to recover the product. The preferred concentration of this salt is from about 0.05 to 0.25 weight percent.

The following examples illustrate the preparation of the hydrocarbylamine salts of oxalic acid.

EXAMPLE I

Di-*t*-C₁₂-C₁₄ Alkylamine Salt of Oxalic Acid

Two moles of *t*-C₁₂ to C₁₄ alkylamine were refluxed with one mole of oxalic acid dihydrate in benzene using a Dean Stark water separator. When the theoretical amount of water had been collected the mixture was concentrated under reduced pressure to recover the product.

Analysis of the product was as follows:

Percent nitrogen (theory) 5.9. Found 5.6. Neutralization No. (theory) 237. Found 212.

EXAMPLE II

Di-*t*-C₁₈-C₂₂ Alkylamine Salt of Oxalic Acid

Two moles of *t*-C₁₈-C₂₂ alkylamine were refluxed with a mole of oxalic acid and the product recovered as in Example I above.

Analysis of the product was as follows: Percent nitrogen (theory) 3.9. Found 3.5. Neutralization (theory) 156. Found 155.

EXAMPLE III

Di-Secondary C₁₁ Alkylamine Salt of Oxalic Acid

Two moles of secondary C₁₁-alkylamine were refluxed with a mole of oxalic acid and the product recovered as in Example I.

Analysis of the product was as follows: Percent nitrogen (theory) 5.7. Found 5.3. Neutralization No. (theory) 227. Found 211.

EXAMPLE IV

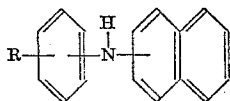
Di-Secondary C₁₅ Alkylamine Salt of Oxalic Acid

Two moles of secondary C₁₅-alkylamine were refluxed with a mole of oxalic acid and the product recovered as in Example I above.

Analysis of the product was as follows: Percent nitrogen (theory) 4.5. Found 3.9. Neutralization No. (theory) 179. Found 166.

Other typical dihydrocarbylamine salts of the invention include di-*t*-octyl amine, di-dodecyl amine, di-stearyl amine, di-(diisobutyl amine), di-(dicyclohexyl amine), di-(diisooamyl amine) and di-(didodecyl amine) oxalate salts.

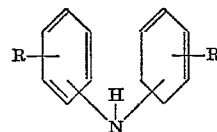
The essential alkyl or alkaryl phenyl naphthylamine component of the invention is represented by the formula:



in which R is an alkyl or alkaryl radical having from about 4 to 12 carbon atoms. This radical can be a straight or branched chain alkyl radical with the tertiary alkyl structure being preferred or it can be an alkaryl radical. The naphthylamine can be either an alpha or beta naph-

thylamine. Specific effective compounds of this class include N-*p*-*t*-octylphenyl- α -naphthylamine, N-(4-cumylphenyl)-6-cumyl- β -naphthylamine, N-(4-cumylphenyl)-6-cumyl- α -naphthylamine, N-*p*-*t*-octylphenyl- β -naphthylamine and the corresponding *p*-*t*-dodecylphenyl, *p*-*t*-butylphenyl, and *p*-dodecylphenyl- α and - β -naphthylamines. The preferred concentration of this component is from about 0.5 to 2.5 percent.

Another essential component of the lubricating oil composition of the invention is a dialkylphenylamine. These compounds are represented by the formula:



in which R is an alkyl radical having from about 4 to 12 carbon atoms. Suitable alkylamines include dioctyldiphenylamine, didecylphenylamine, didodecylphenylamine, dihexyldiphenylamine and similar compounds. Dioctyldiphenylamine is the preferred compound and the preferred concentration is from 0.5 to 2.0 percent.

The final essential component of the lubricating oil composition of the invention is a hydrocarbylphosphate ester, more specifically a trihydrocarbyl phosphate having the formula (RO)₃PO in which R is a hydrocarbyl radical. More specifically R is an alkyl, aryl, alkaryl, cycloalkyl or aralkyl radical or mixture thereof having from 2 to 12 carbon atoms and preferably from 4 to 8 carbon atoms. Effective specific compounds include tricresylphosphate, cresyl diphenylphosphate, triphenylphosphate, tributylphosphate, tri(2-ethylhexyl)-phosphate and tricyclohexyl phosphate. These compounds are preferably present in the lubricating oil composition in a concentration ranging from about 0.5 to 5 percent.

The lubricating oil composition of the invention was tested for its oxidation and corrosion resistance in oxidation-corrosion tests described below:

The 400° F./12 hr. oxidation and corrosion test is conducted in accordance with Method 5308.4 of Federal Test Method and Standard No. 791a (issued Dec. 31, 1961) except for modifications to conform to MIL-L-23699B specifications and the 425° F./48 hr. oxidation and corrosion test conforms to Pratt and Whitney 521B specification. The bath temperature is maintained at 400 and 425±1° F., respectively, instead of at 250° F. and the tests are conducted for periods of 72 hours and 48 hours instead of 168 hours as originally specified.

The ester base oils employed in preparing the lubricating oil compositions tested below comprised pentaerythritol containing a minor amount of dipentaerythritol esterified with mixtures of fatty acids.

Base Oil A consisted of technical grade pentaerythritol ester made from a mixture of carboxylic acid consisting of (mole percent):

	Percent
<i>i</i> -C ₅ -----	8±3
<i>n</i> -C ₅ -----	23±5
<i>n</i> -C ₆ -----	20±5
<i>n</i> -C ₇ -----	27±5
<i>n</i> -C ₈ -----	7±3
<i>n</i> -C ₉ -----	16±3

This ester base oil had the following properties:

Viscosity, cs at 210° F. -----	5.01
Viscosity, cs at 100° F. -----	25.6
Viscosity, cs at -40° F. -----	7005
Viscosity Index -----	140
Flash, ° F. -----	515

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Base Oil B was similar to Base Oil A but consisted of pentaerythritol ester made from the following mixture of carboxylic acids (mole percent):

	Percent
<i>i</i> -C ₅ -----	10±3
<i>n</i> -C ₅ -----	22±5
<i>n</i> -C ₆ -----	7±5
<i>n</i> -C ₇ -----	15±5
<i>n</i> -C ₈ -----	22±5
<i>n</i> -C ₉ -----	17±5
<i>n</i> -C ₁₀ -----	1 Max

Two base fluids were prepared employing the foregoing base oils. These had the following compositions:

Base Fluid C consisted of 1.0 weight percent of *p,p'*-di-tert.-octyldiphenylamine, 1.5 weight percent of N-(4-cumylphenyl) - 6 - cumyl - β - naphthylamine, and 2.0 weight percent tricresylphosphate and the balance Base Oil A referred to above.

Base Fluid D was similar to Base Fluid A above except that it was prepared using Base Oil B.

The Oxidation-Corrosion Test result obtained employing the ester base lubricants of this invention are set forth in Table I below.

TABLE I.—EVALUATION OF DIHYDROCARBYL AMINE SALTS OF OXALIC ACID

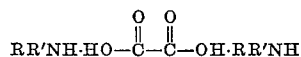
Run	Additive and conc.	Base fluid	Oxidation-corrosion test results							
			400° F./72 hr.			425° F./48 hr.				
			Metal wt. change (mg./cm. ²)		Vis inc. (100° F.)	Tan inc.	Metal wt. change (mg./cm. ²)		Vis. inc.	Tan inc.
1	None	C	-0.50	0.0			21.2	0.93		
2	do	D	-1.29	0.02	25.8	2.36	-1.42	-0.09	25.8	2.66
3	Example I	0.1 C	-0.28	0.0	28.2	1.99	-0.77	-0.02	23.1	1.86
4	Example II	0.1 C	-0.21	0.0	17.8	1.21	0.0	0.0	21.4	1.15
5	Example IV	0.1 D	-0.39	0.0	23.9	1.78	-0.85	0.0	24.6	2.30
6	Example I	0.1 D	-0.21	0.0	26.9	1.25	-0.33	-0.04	28.8	1.80

The working examples of the lubricating oil composition of the invention illustrate novel, operative synthetic ester base lubricant compositions. This invention provides an ester base lubricating oil composition having effective oxidation and corrosion resistance and which overcomes a serious metal staining problem in gas turbine engines.

We claim:

1. A synthetic lubricating oil composition comprising a major portion of an aliphatic ester base oil having lubricating properties formed from the reaction of a pentaerythritol or trimethylolpropane and a saturated hydrocarbyl monocarboxylic acid having from about 2 to 18 carbon atoms per molecule, containing

A. From about 0.005 to 0.5 weight percent of a dihydrocarbylamine salt of oxalic acid represented by the formula:



in which R is a hydrocarbyl radical having from about 8 to about 22 carbon atoms and R' is hydrogen or a hydrocarbyl radical having from 1 to 5 carbon atoms

B. From about 0.3 to 5 percent by weight of the lubricating oil composition of an alkyl or alkaryl phenyl naphthylamine in which the alkyl radical has from 4 to 22 carbon atoms

C. From about 0.3 to 5 percent of a dialkyldiphenylamine in which the alkyl radicals have from 4 to 12 carbon atoms, and

D. From about 0.25 to 10 percent of a trihydrocarbyl phosphate in which said hydrocarbyl radical contains an aryl ring and contains from about 6 to 18 carbon atoms.

2. A lubricating oil composition according to Claim 1 in which said hydrocarbyl radical is an aliphatic hydro-

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carbon radical having from about 12 to about 18 carbon atoms.

3. A lubricating oil composition according to Claim 1 in which said dihydrocarbylamine salt of oxalic acid is di-*t*-C₁₂-C₁₄ alkylamine salt of oxalic acid.

4. A lubricating oil composition according to Claim 1 in which said dihydrocarbylamine salt of oxalic acid is di-*t*-C₁₈-C₂₂ alkylamine salt of oxalic acid.

5. A lubricating oil composition according to Claim 1 in which said dihydrocarbylamine salt of oxalic acid is di-sec-C₁₁ alkylamine salt of oxalic acid.

6. A lubricating oil composition according to Claim 1 in which said dihydrocarbylamine salt of oxalic acid is di-sec-C₁₅ alkylamine salt of oxalic acid.

7. A lubricating oil composition according to Claim 1 containing from about 0.5 to 2.5 percent of a dicumylphenyl-α or β naphthylamine, from about 0.5 to 2.0 percent of dioctyldiphenylamine, and from about 0.5 to 5 percent of a trihydrocarbyl phosphate.

8. A lubricating oil composition according to Claim 1 in which said aliphatic ester base oil is formed from the reaction of pentaerythritol with a mixture of aliphatic acids having from about 5 to 10 carbon atoms.

9. A lubricating oil composition according to Claim 1 in which said aliphatic ester base oil comprises the reaction of pentaerythritol with substantial proportions of iso-valeric, valeric, caproic, heptylic, caprylic and pelargonic acids in which the average acid carbon chain length is between 6 and 7.

10. A lubricating oil composition according to Claim 1 in which said ester base oil is formed from pentaerythritol and saturated aliphatic acids having from 5 to 10 carbon atoms, said naphthylamine is N-(4-cumylphenyl)-6-cumyl-β-naphthylamine at a concentration of 0.5 to 2.5 percent, said dialkyldiphenylamine is dioctyldiphenylamine at a concentration of 0.5 to 2 percent, and said trihydrocarbyl phosphate is tricresyl phosphate at a concentration of 0.5 to 5 percent.

11. A lubricating oil composition according to Claim 1 containing from about 0.05 to 0.25 weight percent of said dihydrocarbylamine salt of oxalic acid.

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HELEN M. S. SNEED, Primary Examiner

U.S. Cl. X.R.

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