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Nebzydoski et al.

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[54] **SYNTHETIC AIRCRAFT TURBINE OIL**

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[52] **U.S. Cl.**..... **252/46.7,** 252/47.5, 252/50, 252/56 S

[51] **Int. Cl.**..... **C10m 1/48**

[58] **Field of Search**..... 252/47.5, 50, 56 S, 51.5 A, 252/49.9, 46.7

[56] **References Cited**

UNITED STATES PATENTS

3,330,763	7/1967	Damrath	252/47.5
3,696,851	10/1972	Randell	252/56 S
3,752,764	8/1973	Sullivan	252/50

FOREIGN PATENTS OR APPLICATIONS

1,180,387	2/1970	Great Britain	252/56 S

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[57] **ABSTRACT**

Synthetic lubricating oil composition comprising a major portion of an aliphatic ester base oil having lubricating properties formed by the reaction of a pentaerythritol or trimethylolpropane and an organic monocarboxylic acid containing (a) from about 0.01 to 2.5 weight percent of an ammonium thiocyanate represented by the formula:

$$RN^{+}R'R''R'''SC^{-}N$$

in which R is a hydrocarbyl or amino-substituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:

$$-R''''\underset{R'''}{\overset{R'}{N}}R''SCN$$

in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' represent hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, (b) from about 0.001 to 0.10 percent of 3-amino-1H-1,2,4-triazole; (c) from about 0.3 to 5 percent of an alkyl or alkaryl phenylnaphthylamine; (d) from about 0.3 to 5 percent of a dialkyldiphenylamine; and (e) from about 0.25 to 10 percent of a hydrocarbyl phosphate ester.

10 Claims, No Drawings

SYNTHETIC AIRCRAFT TURBINE OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with a lubricating oil composition for a gas turbine or jet engine. Gas turbine engines are operated under extreme environmental conditions. The lubricant must be fluid at very low temperatures and at the same time retain its lubricating properties in an engine which produces internal operating temperatures of 450°–550°F. or above. This range of conditions puts such severe stresses on the lubricant that the most advanced mineral lubricating oil compositions as well as many synthetic lubricants cannot be employed for lubricating turbine engines.

Currently, synthetic ester lubricating oil compositions comprising an ester base from pentaerythritol or trimethylolpropane and containing a critically balanced blend of additives are being employed for lubricating gas turbine engines. These ester base lubricating oils are operative over a wide temperature range and exhibit good thermal stability with a high level of oxidation and corrosion resistance. Newer and more powerful gas turbine engines designed to provide advanced levels of supersonic flight are being introduced, however, which will require resistance to substantially higher levels of thermal and oxidative stresses. This situation becomes more critical with respect to military type turbine engines where high gear load-carrying properties are an additional severe requirement.

Description of the Prior Art

U.S. Pat. No. 3,330,764 discloses a synthetic lubricating oil composition having improved load-carrying properties employing a pentaerythritol ester base oil containing in combination an ammonium thiocyanate and a cyclic amine compound of the type represented by phenyl-alpha-naphthylamine.

A copending application, Ser. No. 160,192 filed July 7, 1971 (now U.S. Pat. No. 3,756,952 dated 9/4/73) discloses a synthetic aircraft turbine oil composition containing an ammonium thiocyanate in combination with a polyhydroxyanthraquinone.

A copending application, Ser. No. 361,093 filed concurrently herewith, discloses a synthetic aircraft turbine oil composition containing 3-amino-1H-1,2,4-triazole.

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:

a. an ammonium thiocyanate represented by the formula:

$$RN^{+}R'R''R'''S^{-}CN$$

in which R is a hydrocarbyl or amino-substituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:

$$-R''''\overset{R'}{\underset{R'''}{N}}R''SCN$$

in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' represent hydrogen or a hydrocarbyl group having 1 to 30 carbon atoms,

b. from about 0.001 to 0.10 weight percent of 3-amino-1H-1,2,4-triazole,

c. from about 0.3 to 5 percent by weight of the lubricating oil composition of alkyl or alkaryl derivatives of phenyl α or β naphthalamines in which the alkyl radicals have from 4 to 12 carbon atoms,

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

e. 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.

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 from about 0.01 to 2.5 weight percent of the prescribed ammonium thiocyanate and from about 0.001 to 0.10 weight percent of said 3-amino-1H-1,2,4-triazole, from about 0.5 to 2.0 weight percent of said alkyl or alkaryl derivatives of phenyl-α-or-β-naphthylamine, from about 0.5 to 2.0 weight percent of said dialkyldiphenylamine and from about 0.5 to 5 weight percent of said trihydrocarbyl phosphate.

This invention is based on the discovery that an ester base lubricating oil composition containing the foregoing additive combination has superior load-carrying properties for high gear load applications. While certain ester base lubricating oil compositions containing ammonium thiocyanates in combination with cyclic amines or other additives have good load-carrying properties as shown in the art cited above, the discovery of a novel and critical additive combination in a specific fluid formulation to provide high gear load-carrying properties was surprising.

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, such as dipentaerythritol, tripentaerythritol and tetrapentraerythritol 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, 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 tetracaproate, which is prepared from purified pentaerythritol and crude caproic acid containing other C_{5-10} 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

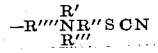
percent pelargonic acids. Another effective ester is the triester of trimethylolpropane in which the trimethylolpropane is esterified with a monobasic acid mixture consisting of 2 percent valeric, 9 percent caproic, 13 percent heptanoic, 7 percent octanoic, 3 percent caprylic, 65 percent pelargonic and 1 percent capric acids. Trimethylolpropane triheptanoate is also a suitable ester base.

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 concentrations from about 90 to 98 percent of the composition.

The ammonium thiocyanate component of the lubricating oil composition of the invention is represented by the formula:

$$RN^{+}R'R''R'''S^{-}CN$$

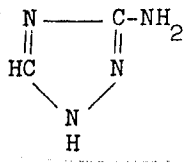
in which R is a hydrocarbyl or amino-substituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:



in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' may be alkyl, cycloalkyl, aryl or mixed hydrocarbyl groups. In the preferred compounds, R is an aliphatic hydrocarbon radical having from 8 to 22 carbon atoms, and R', R'' and R''' are hydrogen or an aliphatic hydrocarbon radical having from 1 to 4 carbon atoms.

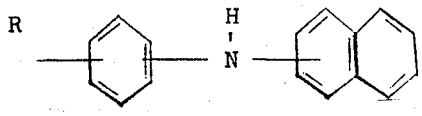
Effective ammonium thiocyanates include bis-(2-ethylhexyl)ammonium thiocyanate, tert. $-C_{18-22}$ alkyl ammonium thiocyanate, sec. $-C_{10-14}$ alkyl ammonium thiocyanate, tert.-octyl ammonium thiocyanate, n-dodecyl ammonium thiocyanate, tert. C_{12-14} alkyl ammonium thiocyanate, nonylammonium thiocyanate, laurylammonium thiocyanate, stearylammonium thiocyanate, dimethyl-2-ethylhexylammonium thiocyanate, dibutyl-octylammonium thiocyanate and N,N'-di-(t-octyl)-1,2-ethanediammonium thiocyanate and N,N'-di-(t-C_{18-22} alkyl)-1,2-ethanediammonium thiocyanate. The ammonium thiocyanate is normally employed at a concentration from about 0.01 to 2.5 weight percent with the preferred amount being from 0.05 to 0.5 percent.

The essential 3-aminotriazole component of the lubricating oil composition of the invention is represented by the formula:



The preferred concentration of the 3aminotriazole is an amount from about 0.005 to 0.05 weight percent.

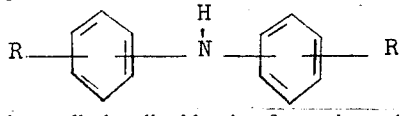
The essential alkyl or alkaryl phenyl naphthylamine component of the invention is represented by the formula:



in which R is an alkyl or alkaryl radical having from about 3 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 alkylaryl radical.

The napthylamine can be either an alpha or beta naphthylamine. Specific effective compounds of this class include N-(p-t-octylphenyl)-α-naphthylamine, N-(4-cumylphenyl)-6-cumyl-B-naphthylamine, N-(p-t-octylphenyl)-α-naphthylamine and the corresponding p-t-dodecylphenyl, p-t-butylphenyl, and p-dodecylphenyl-α-and-B-naphthylamines. The preferred naphthylamines are those in which R is a tertiary alkyl radical having from 6 to 10 carbon atoms. 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 dialkyldiphenylamine. 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 and similar compounds. The preferred class of dialkyl diphenylamines are those in which R is an alkyl radical having from 8 to 10 carbon atoms. 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 i.e., 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 load-carrying properties in the IAE Gear Test which is specified in the U.S. Navy Specification XAS-2354 and British DERD-2497. This test was run at 6000 RPM and at 110°C. in accordance with the Institute of Petroleum Method - 166.

The ester base oil 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 a pentaerylthritol ester made from a mixture of carboxylic acid consisting of (mole percent):

i - C_5	12 ± 3
n - C_5	28 ± 5
n - C_6	11 ± 5
n - C_7	17 ± 5
n - C_8	29 ± 5
n - C_9	12 ± 5
n - C_{10}	1 Max.

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

A Base Blend was prepared from the foregoing Base Oil. This Base Blend consisted of the Base Oil with about 1.0 weight percent p,p'-di-tert-octyldiphenylamine, 1.50 weight percent N-(4-tert.-octylphenyl)-1-naphthylamine and 2.0 weight percent tricresylphosphate. An ammonium thio-cyanate and/or 3-amino-1H-1,2,4-triazole was added to the Base Blend to make up the finished lubricants for testing below.

TABLE I

I.A.E. LOAD CARRYING TEST

Example	Lubricant Composition				I.A.E. Failure Load, pounds
		Salt of Thiocyanic Acid Cenc. Wt. %	Benzotriazole wt. %	3-Amino-1H-1,2,4 triazole, wt. %	
1.	Base Blend	t-C_{18-22} alkyl ammonium thiocyanate 0.1	—	—	58
2.	Base Blend	t-C_{18-22} alkyl ammonium thiocyanate 0.1	0.03	—	58
3.	Base Blend	t-C_{18-22} alkyl ammonium thiocyanate 0.1	—	0.03	68

The foregoing data shows that the lubricant of Run 1 consisting of the Base Blend and 0.1 weight percent of t-C_{18-22} alkyl ammonium thiocyanate had an I.A.E. Failure Load of 58 pounds. A second lubricant, Run 2, consisting of the Base Blend plus 0.1 weight percent of t-C_{18-22} alkyl ammonium thiocyanate and 0.03 weight percent of benzotriazole had an I.A.E. Failure Load of 58 pounds. No improvement in the load carrying property of the lubricant was achieved from the addition of the benzotriazole.

In contrast, a lubricant consisting of the Base Blend plus 0.1 weight percent of t-C_{18-22} alkyl ammonium thiocyanate and 0.03 weight percent of 3-amino-1H-1,2,4-triazole, Run 3, had an I.A.E. Failure Load of 68 pounds. This unexpected improvement is attributed to criticality in the lubricant formulation which enhances the load-carrying property.

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 an organic monocarboxylic acid having from about 2 to 18 carbon atoms per molecule containing:

a. from about 0.01 to 2.5 weight percent of an ammonium thiocyanate represented by the formula:

$$RN^{+}R'R''R'''S^{-}CN$$

in which R is a hydrocarbyl or amino-substitituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:

$$-R''''\underset{R'''}{\overset{R'}{N}}R''SCN$$

in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' represent hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms,

b. from about 0.001 to 0.10 weight percent of 3-amino-1H-1,2,4-triazole,

c. 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 3 to 12 carbon atoms,

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

e. 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 the concentration of said 3-amino-1H-1,2,4-triazole ranges from 0.005 to 0.05 weight percent.

3. A lubricating oil composition according to claim **1** containing from about 0.05 to 0.5 weight percent of said ammonium thiocyanate.

4. A lubricating oil composition according to claim **1** in which said ammonium thiocyanate is tert.-C_{18-22} alkyl ammonium thiocyanate.

5. A lubricating oil composition according to claim **1** in which said ammonium thiocyanate is tert.-C_{12-14} alkyl ammonium thiocyanate.

6. A lubricating oil composition according to claim **1** in which said ammonium thiocyanate is tert.-octyl ammonium thiocyanate.

7. A lubricating oil composition according to claim **1** containing from about 0.3 to 5 percent by weight of N-(4-tert.-octylphenyl)-1-naphthylamine, from about 0.3 to 5 weight percent of p,p'-di-tert.-octyldiphenylamine and from about 0.25 to 10 percent of tricresylphosphate.

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 isovaleric, 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 monooctylphenylalpha 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.

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