United States Patent Office 3,756,952 Patented Sept. 4, 1973

3,756,952

SYNTHETIC AIRCRAFT TURBINE OIL

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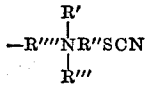
No Drawing. Filed July 6, 1971, Ser. No. 160,192
Int. Cl. C10m 1/38
U.S. Cl. 252—47.5 9 Claims

ABSTRACT OF THE DISCLOSURE

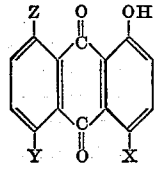
Synthetic lubricating oil composition comprising a major portion of an aliphatic ester base oil having lubricating properties formed by the reaction of a pentaerythritol or trimethylolpropane and an organic monocarboxylic acid containing from about 0.01 to 2.5 weight percent of an ammonium thiocyanate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

$$R\overset{+}{N}R'R''R'''\overset{-}{S}CN$$

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''' represent hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, and from about 0.04 to 2 weight percent of a polyhydroxy-substituted anthraquinone represented by the formula:



in which X, Y and Z each represent hydrogen or a hydroxyl group and at least one of the these is a hydroxyl group.

BACKGROUND OF THE INVENTION

Field of the invention

This invention is concerned with a lubricating oil composition for a gas turbine or jet engine. Gas turbine aircraft engines are operated under extreme environmental conditions. External atmospheric temperatures are generally in the sub-zero range and internal engine temperatures are in the order of 400–500° 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.

Synthetic ester base lubricating oil compositions containing a critically balanced blend of additives are being employed for lubricating gas turbine engines. These ester base oils are operative over a wide temperature range and exhibit good thermal stability, anti-wear, load-carrying and anti-oxidation properties.

With the advent of advanced, more powerful gas turbine engines, higher levels of thermal and oxidative stresses are imposed on the lubricating oil composition. The present invention is directed to an improved synthetic ester base lubricating oil composition.

DESCRIPTION OF THE PRIOR ART

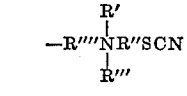
U.S. 3,330,763 discloses a synthetic lubricating oil composition having improved load-carrying properties employing a pentaerythritol ester base oil containing in combination an ammonium thiocyanate and a cyclic amine compound of the type represented by phenyl-alpha-naphthylamine.

SUMMARY OF THE INVENTION

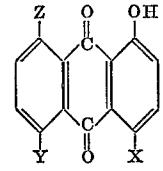
The synthetic lubricating oil composition of the invention comprises a major portion of an aliphatic ester base oil having lubricating properties containing an ammonium thiocyanate represented by the formula:

$$R\overset{+}{N}R'R''R'''\overset{-}{S}CN$$

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''' represent hydrogen or a hydrocarbyl group having 1 to 30 carbon atoms, and a polyhydroxy-substituted anthraquinone represented by the formula:



in which X, Y and Z each represent hydrogen or a hydroxyl group and at least one these is a hydroxyl group.

More specifically, the lubricating oil composition of the invention will consist of an ester base formed by the reaction of a pentaerythritol or trimethylolpropane with an organic monocarboxylic acid, from about 0.01 to 2.5 weight percent of the prescribed ammonium thiocyanate and from about 0.04 to 2.0 weight percent of the prescribed polyhydroxy-substituted anthraquinone.

This invention is based on the discovery that an ester base lubricating oil composition containing the foregoing additive combination has superior load-carrying properties. While certain ester base lubricating oil compositions containing ammonium thiocyanates in combination with cyclic amines have effective load-carrying properties as shown in the art cited above, the discovery of a novel and highly specific additive combination in a particular fluid formulation to provide an unexpected improvement in load-carrying properties was surprising. Critically in the structure of the hydroxyanthraquinone has been established by data showing the ineffectiveness of many of these compounds.

The base fluid component of the lubricant of the invention is an ester-base fluid prepared from a pentaerythritol or trimethylolpropane and a mixture of hydrocarbyl monocarboxylic acids. It is understood that the pentaerythritol class includes the polypentaerythritols, such as dipentaerythritol, tripentaerythritol and tetrapentaerythritol as suitable components of the ester 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, the preferred members having from 5 to 10 carbon atoms. Examples of suitable acids

are acetic, propionic, butyric, valeric, isovaleric, caproic, decanoic, cyclohexanoic, naphthenic, benzoic acid, phenylacetic, tertiary-butylacetic 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 commercially available tetraesters include pentaerythritol tetracaproate, which is prepared from purified pentaerythritol and crude caproic acid containing other C_5–C_{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 trimetholopropane in which the trimetholopropane 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 tripheptanoate, trimethylolpropanepentanoate and trimethylolpropanehexanoate are also suitable ester bases.

The ester base comprises the major portion of the fully formulated synthetic ester base lubricating oil composition. The ester base normally constitute at least 90 percent of the lubricating oil composition and generally will comprise from about 90 to 98 percent of the lubricant.

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

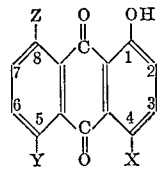
$$R\overset{+}{N}R'R''R'''\overset{-}{S}CN$$

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

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

in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' 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, 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 second essential component of the lubricating oil composition is a polyhydroxy-substituted anthraquinone inhibitor represented by the formula:



in which X, Y and Z each represent hydrogen or a hydroxyl group and at least one of these is a hydroxyl group. There is criticality in the structure of the polyhydroxy-substituted anthraquinone. This compound must have at least two hydroxyl groups and both of these must be attached to the ring carbon atoms in the alpha position to the quinone rings, i.e. on positions 1, 4, 5 and 8. Additional hydroxyl groups may be present without changing the effectiveness of the noted compounds. Compounds having only one hydroxyl group or compounds having more than one hydroxyl group but with only one on the 1, 4, 5 and 8 carbon positions are not effective in the present invention. The specific polyhydroxy-substituted anthraquinones noted above must be employed with the prescribed ammonium thiocyanate to provide the improved lubricating oil composition of the invention.

Examples of effective polyhydroxy-substituted anthraquinones include 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone, 1,2,4-trihydroxyanthraquinone and 1,2,5,8-tetrahydroxyanthraquinone.

The ineffective hydroxy-substituted anthraquinones include 1-hydroxyanthraquinone, 5-hydroxyanthraquinone, 1,2-dihydroxyanthraquinone and 2,6-dihydroxyanthraquinone.

In general, the effective polyhydroxy-substituted anthraquinone inhibitor will be employed in a concentration ranging from about 0.04 to 2.0 weight percent of the lubricating oil composition with the preferred concentration being from 0.05 to 0.25 weight percent. There is criticality in the lower concentration limit for the inhibitor since amounts at 0.035 weight percent concentration do not provide the improvements of the invention.

Base Fluid A in the lubricating oil compositions tested below was a technical grade pentaerythritol containing a minor amount of di-pentaerythritol esterified with a mixture of fatty acids comprising (in mole percent) approximately 38 percent valeric, 13 percent 2-methyl pentanoic, 32 percent n-octanoic and 17 percent pelargonic acid and in which the average acid carbon chain length is about 6.5.

This base fluid had the following properties:

Viscosity, cs. at 210° F.	5.05
Viscosity, cs. at 100° F.	26.0
Viscosity, cs. at −40° F.	7683
Viscosity index	296
Flash, ° F.	505

Base Fluid B was a commercial pentaerythritol tetravalerate fluid.

The lubricating oil composition of the invention and comparison fluids were tested to the Ryder Gear Scuff test designated Federal Test Method Standards 791, test method 6508. The results of this test are given in Table I below.

TABLE I.—THE RYDER GEAR SCUFF TEST

Run	Additives[1]		Ryder Gear Scuff Load, p.p.i.
	Amine salt of thiocyanic acid (wt. percent)	Anthraquinone (wt. percent)	
1	Primene JMT[2] (0.10)	None	3,140
2	Tert.-octyl (0.05)	do	2,900
3	Primene 81R[3] (0.10)	do	3,025
4	None	Quinizarin (0.10)	2,590
5	Primene JMT (0.10)	Alizarin[4] (0.10)	2,940
6	Tert.-octyl (0.05)	Quinizarin[5] (0.035)	2,845
7	do	Quinizarin (0.10)	3,970
8	Primene 81R (0.10)	do	3,385
9	Primene JMT (0.10)	do	3,635

[1] Base Fluid A.
[2] C_{18}–C_{22} tert. alkyl primary amine.
[3] C_{11}–C_{14} tert. alkyl primary amine.
[4] 1,2-dihydroxy anthaquinone.
[5] 1,4-dihydroxy anthraquinone.

The foregoing Ryder Gear Test demonstrates the improved lubricating oil compositions of the invention based on the use of specific anthraquinones in the proper concentration when employed in a synthetic ester base oil with various ammonium thiocyanates. Run 6, in which the inhibitor is quinizarin, demonstrates that there is criticality in the concentration of this component since it is

ineffective at the test concentration. Run 5 illustrates an ineffective anthraquinone. Runs 7, 8 and 9 demonstrate the surprising improvement in the Ryder Gear Scuff Load Test brought about by the lubricating oil compositions of the invention.

The Micros Failure Load Test is conducted on a Caterpillar Corporation friction machine which simulates the rolling and sliding wear on the surfaces of toothed gears. The point of lubricant failure is recorded at the applied load in pounds per square inch. The results of this test are given in Table II below.

TABLE II.—MICROS FAILURE LOADS

Run	Additives [d]		Load at failure (p.p.i.)
	Primene JMT salt of thiocyanic acid (wt. percent)	Anthraquinone (wt. percent)	
1	0.10	None	6,070
2	0.10	Alizarin [a] (0.10)	6,450
3	0.10	1-hydroxyanthraquinone (0.10)	5,650
4	0.10	Quinizarin (0.10)	9,000
5	0.10	Purpurin [b] (0.05)	11,220
6	0.10	Quinalizarin [c] (0.10)	8,640

[a] 1,2-dihydroxyanthraquinone.
[b] 1,2-trihydroxyanthraquinone.
[c] 1,2,5,8-tetrahydroxyanthraquinone.
[d] Base Fluid B.

Runs 2 and 3 in Table II demonstrate substantially unimproved fluids containing 1-hydroxyanthraquinone and 1,2-dihydroxyanthraquinone in combination with the Primene JMT salt of thiocyanic acid. Runs 4 through 6 demonstrate outstanding improvement in the load-carrying property of the fluid of the invention, the improvements running from about 50 percent to 100 percent greater load-carrying capacity than the base fluid (Run 1) and the fluids with 1-hydroxyanthraquinone and alizarin (1,2-dihydroxyanthraquinone).

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:

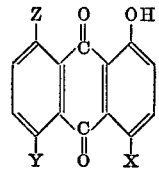
$$R\overset{+}{N}R'R''R'''\overset{-}{S}CN$$

in which R is a hydrocarbyl or an 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, and

(B) from about 0.04 to 2 weight percent of a polyhydroxy-substituted anthraquinone represented by the formula:



in which X, Y and Z each represent hydrogen or a hydroxyl group and at least one of these is a hydroxyl group.

2. A lubricating oil composition according to claim 1 in which said ammonium thiocyanate is 2-ethylhexylammonium thiocyanate and said anthraquinone is quinizarin.

3. A lubricating oil composition according to claim 1 in which said ammonium thiocyanate is tert.-C_{18-22} alkyl ammonium thiocyanate and said anthraquinone is quinizarin.

4. A lubricating oil composition according to claim 1 in which said ammonium thiocyanate is tertiary octyl ammonium thiocyanate and said anthraquinone is quinizarin.

5. A lubricating oil composition according to claim 1 in which said ammonium thiocyanate is diisobutyl ammonium thiocyanate and said anthraquinone is purpurin.

6. A lubricating oil composition according to claim 1 in which said ammonium thiocyanate is tert.-C_{11-14} alkyl ammonium thiocyanate and said anthraquinone is purpurin.

7. A lubricating oil composition according to claim 1 in which said anthraquinone is 1,5-dihydroxyanthraquinone.

8. A lubricating oil composition according to claim 1 in which said anthraquinone is 1,2,5,8-tetrahydroxyanthraquinone.

9. A lubricating oil composition according to claim 1 containing from about 0.05 to 0.5 weight percent of said ammonium thiocyanate and from about 0.05 to 0.25 weight percent of said polyhydroxy-substituted anthraquinone.

References Cited

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DANIEL E. WYMAN, Primary Examiner

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U.S. Cl. X.R.

252—565