United States Patent [19]

Patmore et al.

[11] **3,779,919**

[45] **Dec. 18, 1973**

[54] **SYNTHETIC AIRCRAFT TURBINE OIL**

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[22] Filed: **Aug. 21, 1972**

[21] Appl. No.: **282,181**

[52] **U.S. Cl.** **252/33.6,** 252/47.5, 252/402, 260/306.7

[51] **Int. Cl.** **C10m 1/38,** C10m 1/32

[58] **Field of Search** 252/33.6, 565, 47.5, 252/402; 260/306.7

[56] **References Cited**

UNITED STATES PATENTS

2,796,402	6/1957	Kluge et al.	252/47.5
2,796,403	6/1957	Watson et al.	252/47.5
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[57] **ABSTRACT**

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 containing an amine salt of a substituted rhodanine.

10 Claims, No Drawings

SYNTHETIC AIRCRAFT TURBINE OIL

BACKGROUND OF THE INVENTION

This invention is concerned with a lubricating oil composition for gas turbine or jet engines. Gas turbine engines employed in aircraft are operated under extreme environmental conditions. The lubricating oil must be fluid under sub-zero temperatures and must be thermally stable, non-corrosive and possess load-carrying and anti-wear properties at engine temperatures of 400° to 500°F. or above. The environmental and operating conditions put such a severe stress on the lubricating oil for a turbine engine that the most advanced mineral lubricating oil compositions cannot be employed in these engines. It is conventional to employ synthetic ester-base lubricating oil compositions containing suitable augmenting additive combinations for lubricating turbine engines. The ester-base oils are operative over a wide temperature range and exhibit good thermal stability, anti-wear, and oxidation-resistant properties while providing effective lubrication.

Newer and more powerful gas turbine engines designed to provide advanced levels of supersonic flight are under development. These engines put increasing stresses on the lubricating oil composition and improved oil compositions must be provided to meet the load-carrying, anti-wear, oxidation resistance and corrosion resistance requirements at higher levels of oxidative and thermal stress.

DESCRIPTION OF THE PRIOR ART

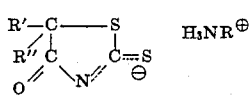
U.S. Pat. No. 2,796,402 discloses grease and lubricating oil compositions having extreme pressure properties containing rhodanine and its five-substituted compounds.

U.S. Pat. No. 2,796,403 discloses grease and lubricating oil compositions including synthetic lubricants having extreme pressure properties containing three-hydrocarbon-substituted rhodanines.

U.S. Pat. No. 2,796,404 discloses lubricating oil compositions including synthetic lubricants of the ester or ether type having extreme pressure and anti-corrosive properties containing 5-alkylaminobenzylidenerhodanine.

SUMMARY OF THE INVENTION

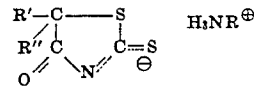
The synthetic lubricating oil composition of the invention comprises a major portion of an aliphatic ester-base oil having lubricating properties formed from the reaction of a pentaerythritol or trimethylolpropane and a mixture of hydrocarbyl monocarboxylic acids containing an effective load-carrying amount of an amine salt of rhodanine represented by the formula:



in which R is a hydrocarbyl radical having from about four to 24 carbon atoms and R′ and R″ represent hydrogen or a hydrocarbyl radical having from about four to 24 carbon atoms. In general, the compounded fluid will also contain an alkylphenyl or alkarylphenyl naphthylamine, a dialkyldiphenylamine, a polyhydroxyanthraquinone and a hydrocarbyl phosphate defined below.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The amine salt of rhodanine suitable for the synthetic lubricating oil composition is represented by the following formula:



where R represents a hydrocarbyl radical having from about four to 24 carbon atoms and R′ and R″ each represent hydrogen or a hydrocarbyl radical having from about four to 24 carbon atoms. The preferred compounds are those in which R is an alkyl or aliphatic radical having from about 12 to 22 carbon atoms and in which R′ and R″ represent hydrogen. The most preferred compounds are those in which R is an aliphatic radical having from about 18 to about 22 carbon atoms and R′ and R″ represent hydrogen.

In general, the prescribed amine salt of rhodanine is prepared by dissolving equimolar portions of a hydrocarbyl amine with rhodanine or a substituted rhodanine in a hydrocarbon solvent and reacting the mixture at a moderately elevated temperature. Reaction temperatures ranging from about room temperature up to about 60°C. are highly effective. The reaction is continued until neutralization has been effected. On completion of the reaction, the solvent is removed to recover the amine salt of rhodanine.

The following examples illustrate the preparation of amine salts of rhodanine which can be employed in the synthetic aircraft turbine oil compositions of this invention.

EXAMPLE I

t-C_{18}-C_{22} Alkyl Primary Amine Salt of Rhodanine

15.7 Grams (0.05 mole) of t-C_{18}-C_{22} alkyl primary amine were slowly added, with stirring, to a solution of 6.65 grams (0.05 mole) of rhodanine in 50 ml. of benzene. The temperature rose from 21° to 33°C. The solution was then heated at 50°C. for about 0.5 hour. The benzene was removed using a rotary evaporator to give 21.6 grams of product. The t-C_{18}-C_{22} alkyl primary amine salt of rhodanine had the following values:

Neutralization No. = 127, calculated 125

percent Nitrogen = 6.2, calculated 6.2

EXAMPLE II

t-C_{12}-C_{14} Primary Alkyl Amine Salt of Rhodanine

19.1 Grams (0.10 mole) of t-C_{12}-C_{14} primary alkyl amine were added dropwise, with stirring, to a solution containing 13.3 grams (0.10 mole) of rhodanine in 70 ml. of benzene. The reaction mixture was heated at 50°C. for one hour and concentrated on a rotary evaporator to afford 32.0 grams of product as a viscous oil. The product analyzed as follows:

percent Nitrogen = 8.8 found, 8.7 calculated

EXAMPLE III

t-Octylamine Salt of Rhodanine

12.9 Grams (0.10 mole) of t-octylamine were added dropwise to a stirred solution containing 13.3 grams (0.10 mole) rhodanine in 70 ml. of benzene. After heating at 50°C. for one hour, the reaction mixture was concentrated under reduced pressure to yield a pale yellow solid. After slurrying with pentane, filtration and drying, 23.5 grams of product were obtained having a melting point of 138° to 142°C. The analysis was as follows:

Neutralization No. = 207, calculated 198
percent Nitrogen = 10.9 found, calculated 10.8

EXAMPLE IV

2-Ethylhexylamine Salt of Rhodanine

26.6 Grams (0.2 mole) of rhodanine and 25.8 grams (0.2 mole) of 2-ethylhexylamine were heated at 150°C., with stirring, for 1 hour. The reaction mixture was diluted with 30 ml. of ethanol, filtered and concentrated under reduced pressure to yield the product as a yellow oil. The analysis was as follows:

Neutralization No. = 262 found, calculated 272
percent Nitrogen = 10.5 found, 10.8 calculated

EXAMPLE V

t-Butylamine Salt of Rhodanine

6.3 Grams (0.1 mole) of t-butylamine were added dropwise to a stirred solution containing 13.3 grams (0.1 mole) of rhodanine in 70 ml. of benzene. The reactants were heated at 50°C. for 1 hour, cooled and filtered to yield 17.0 grams of product having a melting point of 168° to 170°C. The analysis was as follows:

Neutralization No. = 292 found, calculated 272
percent Nitrogen = 12.4 found, 13.5 calculated
percent Sulfur = 32.7 found, 31.0 calculated

Examples of other amine salts of rhodanine which can be employed in the synthetic aircraft turbine oil composition of this invention include the following:

dodecylamine salt of rhodanine
cyclohexylamine salt of rhodanine
n-pentylamine salt of rhodanine
sec-butylamine salt of rhodanine
n-heptylamine salt of rhodanine
t-butylamine salt of 5,5-dibutyl rhodanine
2-ethylhexylamine salt of 5,5-dibutyl rhodanine
t-C_{12}-C_{14} primary alkylamine salt of 5,5-dioctyl rhodanine

The prescribed amine salt of rhodanine is employed in the lubricating oil composition in an amount ranging from about 0.01 to 5 weight percent. In general, amounts ranging from about 0.04 to 0.5 percent are effective and are preferred for imparting load-carrying and corrosion resistance properties to the lubricant composition.

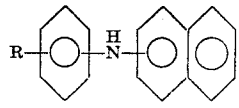
The base fluid component of the lubricant of the invention is an ester-base fluid prepared from pentaerythritol or trimethylolpropane and a mixture of hydrocarbyl monocarboxylic acids. Polypentaerythritols, such as dipentaerythritol, tripentaerythritol and tetrapentaerythritol, can also be employed in 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 two to 18 carbon atoms per molecule, and preferably from about five to 10 carbon atoms. Examples of suitable specific acids are acetic, propionic, butyric, valeric, isovaleric, caproic, decanoic, hexadecanoic, vinylbenzoic, dodecylbenzoic, pelargonic, 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 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 about 50 percent valeric, 12 percent 2-methyl pentanoic, 27 percent caprylic, 15 percent pelargonic, 9 percent heptylic, 5 percent caproic and minor amounts of isovaleric and capric 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, trimethylolpropane tripentanoate and trimethylolpropane trihexanoate are also suitable ester bases.

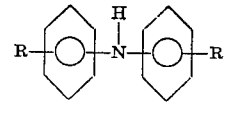
The ester base comprises the major portion of the formulated synthetic ester-base lubricating oil composition. In general, this ester-base fluid is present in a concentration ranging from about 90 to 98 percent of the composition.

The effectiveness of the lubricating oil compositions of the invention is enhanced by the addition of other additives to the oil composition. Alkyl or alkaryl phenyl naphthylamines are highly effective anti-oxidants for synthetic lubricating oils. These compounds are represented by the formula:



in which R is an alkyl or alkaryl radical having from about four 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 naphthylamine can be either an alpha or beta naphthylamine. Specific effective compounds of this class include N-(p-t-octylphenyl)-α-naphthylamine, N-(p-cumylphenyl)-6-cumyl-β-naphthylamine, N-(p-t-octylphenyl)-β-naphthylamine and the corresponding p-t-dodecylphenyl, p-t-butylphenyl, and p-dodecylphenyl-α- and -β-naphthylamines. An effective concentration for this additive is an amount from about 0.5 to 2.5 weight percent.

Another effective anti-oxidant for the lubricating oil composition of the invention is a dialkyldiphenylamine represented by the formula:



in which R is an alkyl radical having from about four to 12 carbon atoms. Examples of these amines include dioctyldiphenylamine, didecyldiphenylamine, didode-

cyldiphenylamine, dihexyldiphenylamine and similar compounds. Dioctyldiphenylamine is the preferred compound and the preferred concentration is from about 0.5 to 2.0 percent.

An effective metal deactivator for a synthetic lubricating oil composition is a polyhydroxyanthraquinone. Effective suitable compounds in this class are the di- or polyhydroxyanthraquinones, such as 1,4-dihydroxyanthraquinone, also known as quinizarin, 1,5-dihydroxyanthraquinone and 1,8-dihydroxyanthraquinone, and the higher polyhydroxy-anthraquinones. The preferred concentration of this component is from about 0.01 to 0.5 weight percent.

A valuable anti-wear component for a synthetic lubricating oil composition is a hydrocarbylphosphate ester, represented by the formula $(RO)_3PO$, in which R is a hydrocarbyl radical having from 2 to 12 carbon atoms. The hydrocarbyl radical can be an alkyl, aryl, alkaryl, cycloalkyl or aralkyl radical of the prescribed carbon chain length, although radicals having from 4 to 8 carbon atoms are preferred. Effective compounds include tricresylphosphate, cresyl diphenylphosphate, triphenylphosphate, tributylphosphate, tri-(2-ethylhexyl)-phosphate and tricyclohexylphosphate. These compounds are generally employed in a 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 and its load-carrying properties in the tests described below. A variety of base fluids containing conventional lubricating oil additives were employed for conducting these tests.

Base Fluid A was a compounded base fluid consisting predominantly of a commercial ester base from pentaerythritol and a mixture of C_5 to C_9 fatty acids containing 0.10 weight percent quinizarin, 1.00 weight percent dioctyldiphenylamine, 1.50 weight percent N-(4-cumylphenyl)-6-cumyl-2-naphthylamine and 2.00 weight percent of tricresylphosphate.

Base Fluid B was a compounded base fluid consisting predominantly of a commercial ester base from pentaerythritol and a mixture of C_5 to C_{10} fatty acids containing 0.10 weight percent quinizarin, 1.00 weight percent dioctyldiphenylamine, 1.50 weight percent N-(4-tert.-octylphenyl)-1-naphthylamine and 2.00 weight percent tricresylphosphate.

Base Fluid C was a compounded base fluid consisting of the commercial ester base from Base Fluid B and containing the additives employed in Base Fluid A.

The 425°F./48-Hour Oxidation and Corrosion Test was conducted in accordance with Method 5308.4 of Federal Test Method and Standard No. 791a (issued December 31, 1969), except for modifications to conform to Pratt and Whitney 521B specifications. The bath temperature is maintained at 425°F. ±1°F. instead of at 250°F. and the test is conducted for a period of 48 hours instead of 168 hours as specified in the original test.

The results of the Oxidation-Corrosion Test are given in Table I below wherein blends containing the additive of the invention are compared to similar blends containing the additive rhodanine.

TABLE I.—425° F./48-HOUR OXIDATION-CORROSION TEST

Run	Blend identification: Additive	Wt. percent	Compounded base fluid	TAN of blend	Metal weight change mg./cm.² Cu	Mg
1	Rhodanine	0.5	A	2.11	−6.14	+0.10
2	do	0.2	A	0.92	−2.16	0
3	Example I	0.1	A	0.15	−0.09	0
4	Example II	0.075	A	0.17	−0.64	0
5	Example III	0.06	A	0.16	−0.78	0
6	Example V	0.04	A	0.16	−0.34	0
7	Example IV	0.06	A	0.11	+0.11	0
8	Rhodanine	0.50	B	2.38	−7.48	+0.23
9	do	0.1	B	0.48	−0.93	−0.04
10	Example I	0.5	B	0.64	−0.35	0
11	do	0.1	B	0.17	−0.54	−0.04
12	do	0.5	C	0.60	−1.29	−0.03
13	do	0.3	C	0.37	−0.81	0
14	do	0.1	C	0.15	−0.27	−0.02

The Ryder Gear Test was employed to demonstrate the load-carrying properties of lubricating oil compositions of the invention. This test was conducted in accordance with the ASTM D–1947 Method, with a slight modification. The results are given in Table II below.

TABLE II

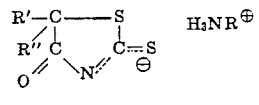
RYDER GEAR LOAD-CARRYING TEST

Run	Blend Identification: Additive	Wt. %	Compounded Base Fluid	Failure Load, ppi
1	Example I	0.1	A	3560
2	Example II	0.075	A	3130
3	Example III	0.06	A	3410
4	Example V	0.04	A	3512
5	Example IV	0.06	A	3230
6	Example I	0.5	B	3408
7	Example I	0.1	B	3180
8	Example I	0.5	C	3710
9	Example I	0.3	C	3540
10	Example I	0.1	C	3230
11	Rhodanine	0.1	B	2910
12	Rhodanine	0.2	A	3180
13	None		A	2740
14	None		B	2689
15	None		C	2775

The foregoing tests demonstrate that the novel synthetic ester-base lubricating oil compositions containing the prescribed amine salts of rhodanine of the invention possess outstanding corrosion-inhibiting and load-carrying properties under high thermal stress encountered in 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 two to 18 carbon atoms per molecule containing from about 0.01 to 5 weight percent of an amine salt of rhodanine represented by the formula:



in which R is a hydrocarbyl radical having from about four to 24 carbon atoms and R′ and R″ represent hydrogen or a hydrocarbyl radical having from about four to 24 carbon atoms.

2. A lubricating oil composition according to claim 1 in which R represents an aliphatic hydrocarbon radi-

cal having from about 12 to 22 carbon atoms and R' and R'' are hydrogen.

3. A lubricating oil composition according to claim **1** containing from about 0.04 to 0.5 weight percent of said amine salt of rhodanine.

4. A lubricating oil composition according to claim **1** in which said amine salt is t-C_{18}-C_{22} alkyl primary amine salt of rhodanine.

5. A lubricating oil composition according to claim **1** in which said amine salt is t-C_{12}-C_{14} alkyl primary amine salt of rhodanine.

6. A lubricating oil composition according to claim **1** in which said amine salt is t-octylamine salt of rhodanine.

7. A lubricating oil composition according to claim **1** in which said amine salt is 2-ethylhexylamine salt of rhodanine.

8. A lubricating oil composition according to claim **1** in which said amine salt is t-butylamine salt of rhodanine.

9. A lubricating oil composition according to claim **1** containing from about 0.5 to 2.5 percent of an alkylphenyl naphthylamine, from about 0.5 to 2.0 percent of a dialkyldiphenylamine, from about 0.01 to 0.5 percent of a polyhydroxyanthraquinone and from about 0.5 to 5 percent of a hydrocarbyl phosphate ester.

10. A lubricating oil composition according to claim **1** in which said ester-base oil is formed from the reaction of pentaerythritol and a mixture of C_5 to C_9 saturated fatty acids.

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