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3,303,131

LUBRICANT COMPOSITIONS

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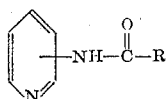
This invention relates to synthetic ester lubricant compositions containing a novel antioxidant combination. In particular, it relates to ester lubricating oils containing a combination of certain amides of aminopyridines and certain organic amines.

Synthetic lubricants have gained recent prominence in the field of lubrication because of stringent requirements of long life under extreme conditions imposed by certain new applications. Synthetic lubricants have low pour points and desirable viscosity characteristics and can generally be used at temperatures considerably above the decomposition temperature of most mineral oils. These oils have found use in jet aircraft, missiles, and the like where wide temperature ranges and extreme operating conditions are likely to be encountered. Proper lubrication of aircraft gas turbines, for example, requires ability to function at bulk oil temperatures as low as -65°F . to as high as 450 to 500°F . for said applications.

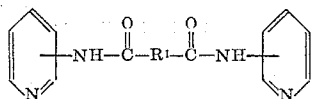
Although these synthetic lubricants are more stable than mineral oils, they nevertheless undergo oxidation when exposed to air, especially when subjected to elevated temperatures such as occur under normal operation. Oxidation stability is further impaired by dissolution of metals under operating conditions. Dissolved metals seem to catalyze oxidative degradation of the lubricant, thereby substantially shortening its useful life. Additives have traditionally been employed in small concentrations to impart resistance to oxidation to these lubricants. Much research effort has been directed to finding additives or combinations of additives which are effective antioxidants for long periods of time yet which do not impart or cause undesirable side effects such as sludge and deposit formation, increased corrosion, viscosity change, discoloration, and so on. Available information regarding mineral oil formulation is generally of little aid in developing successful synthetic lubricants since entirely different side effects are likely to occur under the more extreme conditions to which synthetic lubricants are subjected.

It is known to use various aromatic and heterocyclic amines as additives to increase oxidation stability of synthetic lubricants. These amines are often used alone or in combination. For example, Eickemeyer, U.S. 3,121,691, February 18, 1964, teaches the use of a combination of phenyl-alpha-naphthylamine with an amino quinoline, an aminopyridine, or a dipyrindylamine to reduce oxidation.

The present invention provides a synthetic lubricant having superior oxidation stability imparted by a combination of (A) an amide of an aminopyridine from the group consisting of



and



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where R is an alkyl or aryl group having 1 to about 20 carbons, preferably 2 to 12 carbons, and R' is an alkylene or arylene group having from 2 to about 20, preferably 2 to 12 carbons, and (B) an organic nitrogen-containing antioxidant which is preferably an organic amine. These lubricants have extremely good stability to oxidation, and also provide good cleanliness characteristics.

The amides of aminopyridines used as coadditives of the invention may be amides of either 2-aminopyridine, 3-aminopyridine, or 4-aminopyridine. The 2- and 4-substituted compounds, especially 4-substituted, are preferred. Appropriate concentration of these compounds are from .05 to 5%, preferably 0.1 to 3%, especially 0.1 to 1% by weight of the final lubricating composition. Examples of amides which are used in combination with organic amines are N-4-pyridylpelargonamide, N-2-pyridylpelargonamide, N-4-pyridylvaleramide, N-4-pyridylacetamide, N-3-pyridylvaleramide, N-4-pyridylbenzamide, N-4-pyridyltoluamide, N,N'-di-4-pyridyladipamide, N-2-pyridyl-N'-4-pyridylsebacamide, N,N'-di-2-pyridylphthalamide, N,N'-di-4-pyridylisophthalamide, etc. These additives are well-known compounds which may be prepared by addition of the appropriate carboxylic acid to an aminopyridine.

Organic amines to be used in combination with the above-described amides are primary to tertiary organic amines having from 4 to 12 carbon atoms, preferably containing no elements other than carbon, hydrogen, nitrogen, and sulfur. Preferred amines contain from 4 to 12 carbons, 0 to 2 nitrogens, and 0 to 1 sulfur atoms. They may be aryl amines, diaryl amines, heterocyclic amines, or thiodiarylamines. These compounds are beneficially present in an amount of from about .05 to 5%, preferably 0.1 to 3% by weight of the final lubricating composition. Amounts of about 1.0% are preferred. Examples of suitable aryl amines are naphthyl amine and octylphenylamine. Examples of suitable diaryl amines are phenyl- α -naphthylamine, phenyl- β -naphthylamine, β,β -dinaphthylamine, α,β -dinaphthylamine, and diphenylamine. Examples of suitable heterocyclic amines are 2-aminopyridine, 4-aminopyridine, 2,2'-dipyridylamine, 4,4'-dipyridylamine, 2,4'-dipyridylamine, 2,6-diaminopyridine, phenyl-2-pyridylamine, and naphthyl-2-pyridylamine. Examples of suitable thiodiarylamines are phenothiazine, phenylthio- α -naphthylamine, and phenylthio- β -naphthylamine. Preferred amines are diarylamines, especially phenyl- α -naphthylamine and diphenylamine.

To illustrate the efficacy of the additive combination of the invention, air oxidation tests were conducted on samples of various ester-base lubricants. The tests were carried out at 450°F . by passing a stream of air at the rate of 70 milliliters per minute through a 20-gram sample of the appropriate ester fluid. To more closely approximate actual operating conditions, 20 p.p.m. each of iron or iron and copper, as indicated, were added as octoates. The base stock for all tests was a mixture of 67% C_5 - C_9 acid esters of pentaerythritol and 33% C_5 - C_{10} acid esters of dipentaerythritol. Runs 13-19 were conducted in the additional presence of an extreme pressure additive to illustrate that the unexpected interaction of the amide and the amine persists in the presence of an additional additive; this is important because additional additives may give rise to problems of incompatibility among additives. The EP agent used was a salt of monochloromethylphosphinic acid and C_{18-22} primary amines (referred to in the table as MCMPPA).

Results of the air-oxidation tests are shown in Table I below. Oxidation stability is determined by the length of time, known as the induction period, before which a significant increase in the rate of oxygen absorption occurs.

TABLE I

Run No.	Additives, percent w.	Introduction period, hr.	
		Catalysts	
		Fe	Fe+Cu
1	1.0 phenothiazine (PTZ)		1
2	1.0 phenyl- α -naphthylamine (PAN)	1	2
3	1.0 diphenylamine (DPA)		3
4	0.5 2,2'-dipyridylamine (2,2-DPA)	1	1
5	0.2 MCMPA	0	0
6	0.5 N-4-pyridylpelargonamide	0	1
7	1.0 PAN + 0.5 2,2'-DPA		3
8	1.0 DPA + 0.5 2,2'-DPA		5
9	1.0 PAN + 0.5 N-4-pyridylpelargonamide	1	12
10	1.0 DPA + 0.5 N-4-pyridylpelargonamide		14
11	1.0 PAN + 0.5 N-4-pyridylvaleramide	2	23
12	1.0 DPA + 0.5 N-5-pyridylvaleramide		13
13	1.0 PAN + 0.5 N-4-pyridylacetamide		16
14	1.0 PAN + 0.2 MCMPA		5
15	1.0 PAN + 0.5 N-2-pyridylpelargonamide+0.2 MCMPA	7	4
16	1.0 PAN+0.5 N-4-pyridylpelargonamide+0.2 MCMPA	15	26
17	1.0 DPA+0.5 N-4-pyridylpelargonamide+0.2 MCMPA	15	26
18	1.0 PAN+0.5 N-4-pyridylvaleramide+0.2 MCMPA	6	21
19	1.0 DPA+0.5 N-4-pyridylvaleramide+0.2 MCMPA		27
20	1.0 PAN+0.5 N,N'-di-4-pyridyladipamide+0.2 MCMPA		25
21	1.0 PTZ+0.5 N-4-pyridylvaleramide+0.2 MCMPA		>40
22	0.5 2,2'-DPA+0.5 N-4-pyridylvaleramide+0.2 MCMPA	17	17
		1	>25

An examination of Runs 1-6 indicates that additives of the invention, when used individually, are relatively ineffective under the stringent test conditions. A comparison of Runs 9-13 with Runs 7 and 8 shows that combinations of the invention are considerably more effective even than known synergistic antioxidant combinations. Runs 15-22 illustrate that the cooperative effect of amides and amines of the invention persist in the presence of a known EP agent.

Several compositions of the invention were tested in the Type 2 Bearing Test. This test is used as a final method of evaluating high-temperature synthetic lubricants prior to full scale jet engine testing. It utilizes a circulating oil system and a 100 mm. test bearing similar to many of the bearings used in jet engines. The test is of 100 hours duration and is conducted at 440° F. tank temperature, 400° F. oil-in temperature, and 500° F. bearing temperature. During the test, oil flow to the test bearing is controlled at 600 ml./min. Saturated air enters the bearing compartment at 0.30-0.35 ft.³/min. and is scavenged with the test oil to a 2-gallon test oil tank. Performance of the oil is judged on the basis of resulting deposits and increase in acid number and viscosity. Results of tests of two oils of the invention follow in Table 2. The test oils compared favorably with other available known formulations.

TABLE II.—TYPE II BEARING TEST RESULTS

	1	2
Composition, percent w.:		
Base A ¹	67.0	67.0
Base B ²	33.0	33.0
DPA ³	+1.5	+1.0
2,2'-DPA	+0.1	
MCMPA ³	+0.2	+0.2
N-4-pyridylvaleramide	+0.35	+0.35
Copper dibutyldithiocarbamate	+0.0075	
DCF silicone 200/1,000 cs., p.p.m.	10	10
Azelaic acid	+0.02	
Bearing Rig Test Data:		
Bearing Deposits, Demerits	39.1	22.3
Over-all Deposits, Demerits	103.5	46.8
Acid No. Increase	3.9	5.7
Viscosity Increase (100° F.), percent	110.5	26.2
Filter Sludge (Total), g.	3.2	2.3

¹ C₈-C₁₀ acid esters of pentaerythritol.

² C₈-C₁₀ acid esters of dipentaerythritol.

³ Salt of monochloromethylphosphonic acid and mixed C₁₈-C₂₂ primary amines.

⁴ The amount of this and the subsequent additives present in the compositions is expressed as percent based upon the total weight of Base A and Base B.

Suitable synthetic lubricant base stocks for the practice of the invention are esters of alcohols having 1 to 20, especially 4 to 12 carbons and aliphatic carboxylic acids having from 3 to 20, especially 4 to 12 carbons. The ester base may comprise a simple ester (reaction product of a monohydroxyalcohol and a monocarboxylic acid), a polyester (reaction product of an alcohol and an acid, one of which has more than one functional group), or a complex ester (reaction product of a polyfunctional acid with more than one alcohol, or of a polyfunctional alcohol with more than one acid). Also, excellent synthetic lubricants may be formulated from mixtures of esters, such as major proportions of complex esters and minor amounts of diesters.

Monohydric alcohols suitable for making ester base stocks include methyl, butyl, isooctyl, dodecyl and octadecyl alcohols. "Oxo" alcohols prepared by the reaction of olefins with carbon monoxide and hydrogen are suitable. Neo-alcohols, i.e., alcohols having no hydrogens on the beta carbon atom are preferred. Examples of such alcohols are 2,2,4-trimethylpentanol-1 and 2,2-dimethyl propanol.

Polyalcohols used for the production of base oil esters preferably contain 1 to 12 carbons. Examples of dialcohols are 2-ethyl-1,3-hexanediol, 2-propyl-3,3-heptanediol, 2-butyl-1,3-butanediol, 2,4-dimesityl-1,3-butanediol, and polypropylene glycols having molecular weights of from about 100 to 300. Alcohols having 3, 4, 5 or more hydroxyl groups per molecule are also suitable and are preferred; examples of these polyols are pentaerythritol, dipentaerythritol, and trimethylolpropane. Mixtures of alcohols may also be used.

Suitable carboxylic acids for making the ester base oils include mono- and di-basic aliphatic carboxylic acids. Examples of appropriate acids are butyric, valeric, sebacic, azelaic, suberic, succinic, caproic, adipic, ether suberic, diethyl adipic, oxalic, malonic, glutaric, pentadecanedicarboxylic, diglycolic, thioglycolic, acetic, propionic, caprylic, lauric, palmitic, pimelic, and mixtures thereof. Preferred acids are sebacic, azelaic, glutaric, adipic, and their mixtures.

Examples of suitable ester base oils are ethyl palmitate, ethyl laurate, butyl stearate, di-(2-ethylhexyl) sebacate, di-(2-ethylhexyl) azelate, ethyl glycol dilaurate, di-(2-ethylhexyl) phthalate, di-(1,3-methylbutyl) adipate, di-(1-ethylpropyl) azelate, diisopropyl-oxylate, dicyclohexyl sebacate, glycerol tri-n-heptate, di(undecyl) azelate, and tetraethylene glycol di-(2-ethylene caproate), and mixtures thereof. An especially preferred mixture of esters consists of about 50 to 80% wt. bis(2,2,4-trimethylphenyl) azelate and 20 to 50% wt. 1,1,1-trimethylpropyl propane triheptanoate.

Especially preferred esters for use as base stocks in the present invention are esters of monocarboxylic acids having 3 to 12 carbons and polyalcohols such as pentaerythritol, dipentaerythritol, and trimethylolpropane. Examples of these esters are pentaerythrityl butyrate, pentaerythrityl tetrabutrate, pentaerythrityl tetravalerate, pentaerythrityl tetracaproate, pentaerythrityl dibutyrate, pentaerythrityl butyratecaproate, pentaerythrityl butyratedivalate, pentaerythrityl butyrate trivalerate, pentaerythrityl butyrate tricaproate, pentaerythrityl tributyratcaproate, mixed C₄-C₁₀ saturated fatty acid esters of pentaerythritol, dipentaerythrityl hexavalerate, dipentaerythrityl hexacaproate, dipentaerythrityl hexaheptate, dipentaerythrityl hexacapyrate, dipentaerythrityl tributyratcaproate, dipentaerythrityl trivalerate trinonylate dipentaerythrityl mixed hexaesters of C₄-C₁₀ fatty acids and trimethylolpropane heptylate. Pentaerythrityl esters of mixtures of C₄-C₁₂ acids are excellent base oils, and are commercially available from Hercules Chemical Company.

Ester oils may be prepared by simple reaction of the alcoholic and acidic reactants in proportions suitable for producing the desired product; preparation preferably takes place in a solvent such as an aromatic hydrocarbon,

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and in the presence of a catalyst, such as HCl, HF, HBr, H₂SO₄, H₃PO₄, SCl₂, BF₃, etc. Preparation of suitable esters is described in Eickemeyer, U.S. 3,038,859, issued June 12, 1962, and Young, U.S. 3,121,109, issued February 11, 1964.

Compositions of the invention may also contain other additives to further improve properties of the oil. Examples of other such additives are EP agents, viscosity index improvers, anticorrosion agents, detergents, etc.

Some specific embodiments of the compositions of the invention are as follows:

Composition 1

Base A:	Percent weight	
Bis(2,2,4-trimethylpentyl) azelate	60	15
1,1,1-trimethylpropane triheptanoate	40	
Phenyl- α -naphthylamine	1	
N-4-pyridylpelargonamide	0.5	
Salt of mixed C ₁₈ -C ₂₄ primary amines and monochloromethylphosphonic acid (MCMPPA)	0.2	20

Composition 2

Base B:	Percent weight	
C ₄ -C ₇ acid esters of pentaerythritol	60	
C ₈ -C ₁₀ acid esters of dipentaerythritol	40	25
Diphenylamine	1	
N,N'-di-4-pyridyladipamide	0.5	
Tricresylphosphate	0.5	

Composition 3

Base A:	Percent weight	
Phenothiazine	1	30
N-2-pyridylpelargonamide	0.5	
Chlorinated diphenyl	0.5	

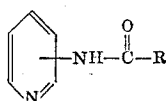
Composition 4

Base B:	Percent weight	
Phenyl- α -naphthylamine	1	35
N-4-pyridylvaleramide	0.5	
MCMPPA	0.2	40

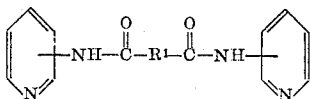
We claim as our invention:

1. A lubricating composition comprising a major amount of a synthetic ester base oil and

(1) 0.05 to 5% by weight of an amide selected from the group consisting of



and



wherein R is selected from alkyl and aryl having from 1 to about 20 carbons, and R' is selected from alkylene and arylene having from 2 to about 20 carbons, and

(2) 0.05 to 5% by weight of an amine selected from the group consisting of arylamines, diarylamines, heterocyclicamines and thiodiarylamines having from 4 to 12 carbon atoms.

2. The composition of claim 1 wherein the organic amine is a diarylamine.

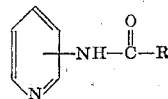
3. The composition of claim 1 wherein the organic amine is a thiodiarylamine.

4. The composition of claim 2 wherein the diarylamine is selected from the group consisting of phenyl- α -naphthylamine and diphenylamine.

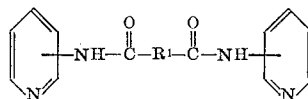
5. A lubricating composition comprising a major amount of a synthetic ester base oil and

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(1) 0.1 to 3% by weight of an amide selected from the group consisting of



and

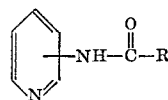


wherein R is selected from alkyl and aryl having from 1 to about 20 carbons, and R' is selected from alkylene and arylene having from 2 to about 20 carbons, and

(2) 0.05 to 5% by weight of an amine selected from the group consisting of arylamines, diarylamines, heterocyclicamines and thiodiarylamines having from 4 to 12 carbon atoms.

6. A lubricant composition comprising a major amount of a synthetic ester base oil and

(1) 0.01 to 3% by weight of an amide of the formula



wherein R is selected from the group consisting of alkyl and aryl having from 1 to about 20 carbons, and

(2) 0.05 to 5% by weight of an amine selected from the group consisting of arylamines, diarylamines, heterocyclicamines and thiodiarylamines having from 4 to 12 carbon atoms.

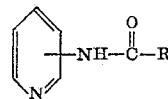
7. The composition of claim 6 wherein the pyridyl group is substituted in the 2-position.

8. The composition of claim 6 wherein the pyridyl group is substituted in the 4-position.

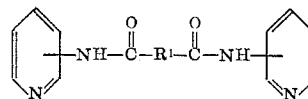
9. The composition of claim 6 wherein the amine is diarylamine.

10. A lubricant composition comprising a major amount of a pentaerythritol ester base oil, and

(1) 0.01% to 3% by weight of an amide selected from the group consisting of



and



wherein R is selected from alkyl and aryl having from 1 to about 20 carbons, and R' is selected from alkylene and arylene having from 2 to about 20 carbons, and

(2) 0.05 to 5% by weight of a diarylamine.

11. The composition of claim 10 wherein the diaryl amine is phenyl- α -naphthylamine.

12. The composition of claim 10 wherein the amide is N-4-pyridylpelargonamide.

13. The composition of claim 12 wherein the diarylamine is phenyl- α -naphthylamine.

14. The composition of claim 12 wherein the diarylamine is diphenylamine.

15. The composition of claim 10 wherein the amide is N-4-pyridylvaleramide. 5

16. The composition of claim 15 wherein the diarylamine is phenyl- α -naphthylamine.

17. The composition of claim 15 wherein the diarylamine is diphenylamine.

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