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LUBRICANT COMPOSITIONS

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This invention relates to synthetic ester lubricant compositions containing a novel antioxidant combination. More particularly, this invention relates to ester lubricating oils containing a combination of diphenylamine and a dipyridylamine.

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. These new lubricants have low pour points and desirable viscosity characteristics and can tolerate 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.

Although synthetic lubricants are in general 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, etc. Available information regarding mineral oil formulations is generally of little aid in developing successful synthetic lubricants since different and more drastic 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-α-naphthylamine with an aminoquinoline, an aminopyridine, or a dipyridylamine to reduce oxidation.

The present invention provides an improved ester base lubricant composition containing diphenylamine and a dipyridylamine in minor amounts effective to impart increased oxidation stability to the lubricant. Preferred dipyridylamines are unsubstituted compounds, preferably 2,2′-dipyridylamine and 4,4′-dipyridylamine, especially the former. Each additive is advantageously present in an amount from about 0.01 to 5% by weight of the final lubricating composition, preferably 0.1 to 3% by weight of the final composition. The presence of both additives is essential to the practice of the invention.

The present invention provides a combination of oxidation inhibitors which is not only surprisingly superior to the individual inhibitors but which is also remarkably more effective than other known synergistic combinations of inhibitors, such as the combination of phenyl-α-naphthylamine and 2,2′-dipyridylamine disclosed by Eickemeyer, cited above.

To illustrate the efficacy of the additive combination of the invention, air oxidation tests were conducted on samples of various ester-based fluids representative of the invention and of the prior art. 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. In all runs, 20 p.p.m. each of iron and copper, added as octoates, were used as catalyst. The oxidation stability of the oil is determined by the length of time, known as the induction period, before which a significant increase in the rate of oxygen absorption occurs. The results of the air oxidation tests are shown in Table I below.

TABLE I.—AIR OXIDATION TESTS

Run No.	Base Oil	Additives, percent w.	Induction Period, hr.
1	Base "A" [a]	1.0 phenyl-α-naphthylamine (PAN)	1
2	do	1.0 diphenylamine (DPA)	3
3	do	0.5 2,2′-dipyridylamine (22DPA)	1
4	do	0.2 M/J [b]	0
5	do	1.0 PAN+0.5 22DPA	4
6	do	1.0 DPA+0.5 22DPA	12
7	do	0.5 22DPA+0.2 M/J	4
8	do	1.0 PAN+0.5 22DPA+0.2 M/J	7
9	do	1.0 DPA+0.5 22DPA+0.2 M/J	24
10	Base "B" [c]	1.0 PAN+0.5 22DPA	3
11	do	1.0 DPA+0.5 22DPA	5
12	do	1.0 PAN+0.2 M/J	5
13	do	1.0 PAN+0.5 22DPA+0.2 M/J	4
14	do	1.0 DPA+0.5 22DPA+0.2 M/J	16

[a] Pentaerythrityl tetraester of mixed C_5–C_9 alkanoic acids.
[b] An extreme pressure agent consisting of a mixed salt of monochloromethyl phosphonic acid and tert-C_{18}–C_{22} alkyl primary amines.
[c] 67% Base "A" plus 33% dipentaerythrityl hexaester of mixed C_5–C_{10} alkanoic acids.

A comparison of Runs 1 through 4 indicates that none of the additives used herein has any substantial antioxidant activities by itself. The phosphonic acid salt, a known EP agent generally present in the amount of about .01–3% wt., has essentially no antioxidant activity. Runs 5, 6, 10 and 11 indicate that the combination of the invention, when tested in the presence of soluble metal, shows far greater antioxidant activity than the known synergistic combination of PAN and 2,2-dipyridylamine. Runs 7 to 9 and 12 to 14 illustrate that in the presence of the EP agent, the effectiveness of the combination of the invention is still further enhanced, rather than being detrimentally affected as might be expected. Thus, in each case the combination of the invention is surprisingly superior to other similar known synergistic combinations.

In addition to the air oxidation tests, a lubricant representative of the invention was compared with one representative of the prior art in the Pratt and Whitney Type II Bearing Test. The formulations were identical except that

the oil of the invention contained 1% w. diphenylamine whereas the oil representative of the art contained 1% w. phenyl-α-naphthylamine. The base oil was in each case a mixture of 67% w. pentaerythrityl tetraester of mixed C_5–C_9 alkanoic acids and 33% w. dipentaerythrityl hexaester of mixed C_5–C_{10} alkanoic acids.

The Type II Bearing Test is employed 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 millimeter 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 enters the bearing compartment at 0.30–0.35 ft.³/min. and is scavenged with the test oil to a two-gallon test oil tank. Performance of the oil in this test is judged on the basis of resulting deposits and increase in acid number and viscosity. The results of the tests are shown in Table II below. Composition I represents the known composition (combination of PAN and 2,2′-dipyridylamine antioxidants), and Composition II represents an oil of the invention.

TABLE II.—BEARING TEST DATA

	Composition I	Composition II
Additives, percent w.:		
PAN	+1.0	
2,2′-dipyridylamine	+0.5	+0.5
Diphenylamine		+1.0
MCMPA/JMT salt	+0.2	+0.2
Copper dibutyldithiocarbamate	+0.0075	+0.0075
DCF 200/1000 cs., p.p.m.	+10	+10
Type 2 Bearing Test Data:		
Deposit, demerits:		
Bearing	42	25
Over-all	84	73
Filter sludge (total), grams	3.5	2.0
Acid no increase	6.1	6.8
Viscosity increase (100° F.), percent	215	211

From the above table it is apparent that the additive combination of the invention provides significantly lower sludge and deposit formation than the additive combination of the art.

Suitable synthetic lubricants based on the practice of the invention are esters of alcohols having 1 to 20, especially 4 to 12 carbon atoms and aliphatic carboxylic acids having from 3 to 20, especially 4 to 12 carbon atoms, and mixtures thereof. The ester base may be a simple ester (reaction product of a monohydroxy alcohol 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. Neoalcohols, i.e., alcohols having no hydrogens on the beta carbon atoms are preferred. Examples of such alcohols are 2,2,4-trimethylpentanol-1 and 2,2-dimethyl propanol.

Polyaclohols 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, ethyl suberic, diethyl adipic, oxalic, malonic, glutaric, pentadecanedicarboxylic, diglycolic, thiodiglycolic, 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, diisopropyloxylate, dicyclohexyl sebacate, glycerol tri-n-heptoate, 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-trimethylpentyl) azelate and 20 to 50% wt. 1,1,1,-trimethylyl propane triheptanoate.

Especially preferred esters for use as base stocks in the present invention are esters of monocarboxylic acids havings 3 to 12 carbons and polyalcohols such as pentaerythritol, dipentaerythritol, and trimethylolpropane. Examples of these esters are pentaerythrityl butyrate, pentaerythrityl tetrabutyrate, pentaerythrityl tetravalerate, pentaerythrityl tetracaproate, pentaerythrityl dibutyratedicaproate, pentaerythrityl butyratecaproate divalerate, pentaerythrityl butyrate trivalerate, pentaerythrityl butyrate tricaproate, pentaerythrityl tributyratecaproate, mixed C_{4-10} saturated fatty acid esters of pentaerythritol, dipentaerythrityl hexavalerate, dipentaerythrityl hexacaproate, dipentaerythrityl hexaheptoate, dipentaerythrityl hexacaprylate, dipentaerythrityl tributyratecaproate, dipentaerythrityl trivalerate trinonylate, dipentaerythrityl mixed hexaesters of C_{4-10} fatty acids and trimethylolpropane heptylate. Pentaerythritol esters of mixtures of C_4–C_{12} 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, and in the presence of a catalyst, such as HCl, HF, HBr, H_2SO_4, H_3PO_4, $SOCl_2$, BF_3, 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.

The lubricating compositions of the invention may also contain other additives such as EP agents, VI improvers, anti-corrosion agents, etc., to improve other properties of the oil. Some specific embodiments of the compositions of the invention are as follows:

Composition I

60% w. C_5–C_9 acid esters of pentaerythritol
40% w. C_5–C_{10} acid esters of dipentaerythritol
+1% w. diphenylamine
+0.5% w. 2,2′-dipyridylamine
+0.2% w. salt of mixed C_{18}–C_{24} primary amines and monochloromethyl phosphonic acid (M/J)

Composition II

Composition I+0.0075% Cu. dibutyldithiocarbamate
+0.02% w. azelaic acid+10 p.p.m. DC 200/1000 silicone fluid

Composition III

60% w. bis(2,2,4-trimethylpentyl) azelate
40% w. 1,1,1-trimethylyl propane triheptanoate
1.5% w. diphenylamine
0.5% w. 2,2′-dipyridylamine
0.2% w. M/J

Composition IV

100% w. diisooctyl azelate
+1.0% w. diphenylamine
+0.5% w. 2,2'-dipyridylamine

We claim as our invention:

1. A lubricant composition comprising a major amount of a synthetic ester lubricating oil, .01% to 5% by weight of diphenylamine, .01% to 5% by weight of dipyridylamine, and .01% to 3% by weight of a mixed salt of monochloromethylphosphonic acid and tert-C_{18}–C_{22} alkyl primary amines.

2. The lubricant composition of claim 1 wherein the dipyridylamine is 2,2'-dipyridylamine.

3. The lubricant composition of claim 1 wherein the dipyridylamine is 4,4'-dipyridylamine.

4. A lubricant composition comprising a major amount of a pentaerythrityl tetraester of C_4–C_{12} aliphatic carboxylic acids, .01% to 5% by weight of diphenylamine, .01% to 5% by weight of dipyridylamine and .01% to 3% by weight of a mixed salt of monochloromethylphosphonic acid and tert-C_{18}–C_{22} alkyl primary amines.

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