United States Patent Office 3,226,324
Patented Dec. 28, 1965

3,226,324

LUBRICANT COMPOSITION CONTAINING PHENOTHIAZINE AND DIPYRIDYLAMINE

Daniel B. Eickemeyer, Park Forest, Ill., assignor to Sinclair Research, Inc., Wilmington, Del., a corporation of Delaware

No Drawing. Filed Feb. 19, 1962, Ser. No. 174,251
10 Claims. (Cl. 252—47.5)

This application is a continuation-in-part of my application Serial No. 34,375, filed June 7, 1960, now abandoned.

This invention relates to ester-based lubricant compositions containing a novel combination of base oil-soluble additive agents. More particularly, the present invention relates to ester-based synthetic lubricant compositions which exhibit increased oxidation resistance.

Organic compounds, such as lubricating oils, undergo oxidation upon exposure to air. This process is accentuated by elevated temperatures such as occur in engines and other operating machinery. When such organic compositions are used as motor or machinery lubricants, their stability is still further drastically reduced due to their contact with metal surfaces which give up metallic particles to the lubricant. Such abraded or dissolved metals or metal salts appear to act as oxidation catalysts in the lubricant causing the formation of primary oxidation products which in turn cause further degradation of the organic compounds present in the composition. In addition, water also causes corrosion of metallic surfaces and accentuates oxidation of the lubricant.

Problems of this nature are encountered in mineral oils but appear to be particularly troublesome in synthetic oleaginous fluids exemplified by esters. Ordinarily, these synthetic ester fluids can be effectively inhibited against oxidation by the us of small amounts of additives. However, in the presence of certain metals and metal compounds often occurring in the lubricants, particularly as aforementioned, through contact with metal surfaces such as iron, the effectiveness of the additives is greatly reduced.

The present invention provides a synthetic ester-based lubricant containing phenothiazine and dipyridylamine.

If desired, there may also be added to the composition of the present invention a minor amount of aminoquinoline, aminopyridine or mixtures thereof. The additives of the present invention are used in minor amounts sufficient to retard oxidation of the lubricants at temperatures in excess of 400° F. even when the lubricant contains oxidation-promoting concentrations of iron. Iron as used in the present invention includes metallic iron and inorganic and organic compounds of iron acknowledged as oxidation catalysts.

The phenothiazine-dipyridylamine additive combination of the present invention provides ester-based fluids with excellent oxidation resistance but in the presence of metal contaminants such as iron, larger amounts of the phenothiazine and/or dipyridylamine may be needed, the exact amount depending on the particular base fluid employed, the amount of metal present, etc. In these cases, the larger amount of dipyridylamine or phenothiazine can be replaced in part with aminopyridine or aminoquinoline. In any event it is preferred to have at least about 0.3 or even 0.5% by weight of each inhibitor used on a total inhibitor concentration of at least about 1.5% or even at least about 2% by weight of the final composition.

The phenothiazine of the present invention can be present in amounts of about .01 to 5 percent by weight of the final composition with a preferred amount being from about 0.3 or 0.5 to 2% and the phenothiazine may be substituted as with alkyl groups. The dipyridylamine

additive can be ring-substituted, as for example with alkyl groups, and can be present in amounts from about 0.10 to 5 percent by weight of final composition, preferably about 0.3 to 2 weight percent. The preferred dipyridylamine is 2,2'-dipyridylamine.

The preferred aminoquinolines for use in the present invention are 3-aminoquinoline and 8-aminoquinoline and their ring-substituted derivatives, e.g., alkyl-substituted. Among the useful aminopyridines are 2-aminopyridine and the ring-substituted, e.g., alkyl-substituted, aminopyridines. The aminoquinolines or aminopyridines when employed, can be added in amounts from about .01 to 5% by weight of the final composition with the preferred amount being from about 0.3 or 0.5 to 2% by weight of the final composition. The aminoquinoline or aminopyridine additive is normally added to the ester-based lubricant along with the phenothiazine. For best results the relative concentrations of the additive will vary with the particular ester lubricant employed and will also be dependent upon the characteristics of the final lubricant composition desired. Normally it is preferred that at least about 1.5 parts of dipyridylamine and at least about 0.5 part of aminoquinoline or aminopyridine, when employed, to 1 part of phenothiazine be used. Increasing the amounts of dipyridylamine, aminoquinoline or aminopyridine will generally be beneficial.

The lubricant composition of this invention includes as the major component a base oil which is an ester of lubricating viscosity which may be, for instance, a simple ester or compounds having multiple ester groupings, such as complex esters, polyesters or diesters. These esters are made from mono- and polyhydroxy aliphatic alcohols and aliphatic carboxylic acids, frequently of about 4 to 12 carbon atoms; aliphatic including cycloaliphatic. It is preferred that the terminal ester monohydric alcohol residues of these fluids be of a non-neomonohydric alcohol, i.e., contains at least one hydrogen atom on the beta carbon. Ester fluids having terminal alcohol groups provided by neo-monohydric alcohols, i.e., an alcohol whose beta carbon atom contains no hydrogen atoms, have been found to be easily inhibited against oxidation by phenothiazine and little protection beyond that afforded by phenothiazine alone may be obtained upon addition of the dipyridylamine component. In the cases where the lubricant was easily inhibited with phenothiazine alone, the terminal alcohol groups also contained a tertiary hydrogen atom.

The reaction product of a monohydroxy alcohol and a monocarboxylic acid is usually considered to be a simple ester. A diester is usually considered to be reaction product of 1 mole of a carboxylic acid, say of 6 to 10 carbon atoms, with 2 moles of a monohydric alcohol or 1 mole of a glycol of 4 to 10 carbon atoms with two moles of a moncarboxylic acid of 4 to 10 carbon atoms. The diesters frequently contain from 20 to 40 carbon atoms. One complex ester is of the type

X—Y—Z—Y—X

in which X represents a monohydric alcohol residue, Y represents a dicarboxylic acid residue and Z represents a glycol residue and the linkages are ester linkages. Those esters, wherein X represents a monoacid residue, Y represents a glycol residue and Z represents a dibasic acid residue are also considered to be complex esters. The complex esters often have 30 to 50 carbon atoms. Polyesters, or "polyester, bright stocks" can be prepared by direct esterification of dibasic acids with glycols in about equimolar quantities. The polyesterification reaction is usually continued until the product has a kinematic viscosity from about 15 to 200 centistokes at 210° F., and preferably 40 to 130 centistokes at 210° F.

Although each of these products in itself is useful as a lubricant, they are particularly useful when added or blended with each other in synthetic lubricant compositions. These esters and blends have been found to be especially adaptable to the conditions to which turbine engines are exposed, since they can be formulated to give a desirable combination of high flash point, low pour point, and high viscosity at elevated temperatures, and need contain no additives which might leave a residue upon volatilization. In addition, many complex esters have shown good stability to shear. Natural esters, such as castor oil may also be included in the blends, as may be up to about 1 percent or more by weight of a foam inhibitor such as a methyl silicone polymer or other additives to provide a particular characteristic, for instance, extreme pressure or load carrying agents, corrosion inhibitors, etc., can be added.

Typical synthetic lubricants may be formulated essentially from a major amount (about 60–85%) of a complex ester and a minor amount (about 15–40%) of a diester, by stirring together a quantity of diester and complex ester at an elevated temperature, altering the proportions of each component until the desired viscosity is reached. Polyesters can be employed to thicken diester base stocks to increase the load carrying capacity of the base diester oil. The polyester will generally not comprise more than about 50 weight percent of the blend, preferably about 20 to 35 weight percent. Usually the amount of the polyester employed in any blend would be at least about 5 percent, and the majority of the lubricant is a diester. Other polymers such as Acryloids may be added as thickeners to the esters, generally the simple esters such as the above diesters, to obtain a base oil of desired viscosity. The Acryloids are polymers of mixed C_4 to C_{18} esters of methacrylic acid having 10,000 to 20,000 molecular weight. Advantageously the final lubricating oil composition would have a maximum viscosity at —40° F. of about 13,000 centistokes and a minimum viscosity of about 7.5 centistokes at 210° F.

The monohydric alcohols employed in these esters usually contain less than about 20 carbon atoms and are generally aliphatic. Preferably the alcohol contains up to about 12 carbon atoms and is of a non-neo structure at the beta carbon atom, i.e., has at least one hydrogen on the beta carbon atom. Useful aliphatic alcohols include butyl, hexyl, methyl, iso-octyl and dodecyl alcohols, C_{13} oxo alcohols and octadecyl alcohols. C_8 to C_{10} branched chain primary alcohols are frequently used to improve the low temperature viscosity of the finished lubricant composition. Alcohols such as n-decanol, 2-ethylhexanol, "oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products such as diisobutylene and C_7 olefins, ether alcohols such as butyl carbitol, tripropylene glycol mono-isopropyl ether, dipropylene glycol mono-isopropyl ether, and products such as "Tergitol 3A3," which has the formula $C_{13}H_{27}O(CH_2CH_2O)_3H$, are suitable alcohols for use to produce the desired lubricant. Iso-octanol and iso-decanol are alcohol mixtures made by the oxo process from C_3 to C_4 copolymer heptenes. The cut which makes up isa-octanol usually contains about 17% 3,4-dimethylhexanol; 29% 3,5-dimethylhexanol; 25% 4,5-dimethylhexanol; 1.4% 5,5-dimethylhexanol; 16% of a mixture of 3-methylheptanol and 5-ethylheptanol; 2.3% 4-ethylhexanol; 4.3% α-alkyl alkanols and 5% other materials.

Generally, the glycols contain from about 4 to 12 carbon atoms; however, if desired they could contain a greater number. Among the specific glycols which can be employed are 2-ethyl-1,3-hexandiol, 2-propyl-3,3-heptanediol, 2-methyl - 1,3 - pentanediol, 2-butyl-1,3-butanediol, 2,4-diphenyl-1,3-butanediol, and 2,4-dimesityl-1,3-butanediol. In addition to these glycols, other glycols may be used, for instance, where the alkylene radical contains 2 to 4 carbon atoms such as diethylene glycol, dipropylene glycol and other glycols up to 1000

to 2000 molecular weight. The most popular glycols for the manufacture of ester lubricants appear to be polypropylene glycols having a molecular weight of about 100–300 and 2-ethyl hexanediol. The 2,2-dimethyl glycols, such as neopentyl glycol have been shown to impart heat stability to the final blends. Minor amounts of other glycols or other materials can be present as long as the desired properties of the product are not unduly deleteriously affected.

Aside from glycols, the esters may be made from polyhydric alcohols of more than two hydroxyl groups, e.g. tri- and tetrahydroxy aliphatic alcohols having about 4 to 12 carbon atoms, preferably about 5 to 8 carbon atoms; for instance pentaerythritol, trimethyolpropane and the like. Particularly suitable ester base oils are formed when these alcohols are reacted with monocarboxylic acids having about 4 to 12 carbon atoms, preferably 4 to 9 carbon atoms. It is preferred that the reaction be conducted so as to substantially completely esterify the acids.

One group of monocarboxylic acids includes those of 8 to 24 carbon atoms such as stearic, lauric, etc. The carboxylic acids employed in making ester lubricants will often contain from about 4 to 12 carbon atoms. Suitable acids are described in U.S. Patent No. 2,575,195 and include the aliphatic dibasic acids of branched or straight chain structures which are saturated or unsaturated. The preferred acids are the saturated aliphatic carboxylic acids containing not more than about 12 carbon atoms, and mixtures of these acids. Such acids include succinic, adipic, suberic, azelaic and sebacic acids and "isosebasic" acid which is a mixture of α-ethyl suberic acid, α,α'-diethyl adipic acid and sebacic acid. This composite of acids is attractive from the viewpoint of economy and availability since it is made from petroleum hydrocarbons rather than the natural oils and fats which are used in the manufacture of many other dicarboxylic acids, which natural oils and fats are frequently in short supply. The preferred dibasic acids are sebacic and azelaic or mixtures thereof. Minor amounts of adipic used with a major amount of sebacic may also be used with advantage.

Various useful ester base oils are disclosed in U.S. Patent Nos. 2,499,983, 2,499,984, 2,575,195, 2,575,196, 2,703,811, 2,705,724 and 2,723,286. Generally, the synthetic base oils consist essentially of carbon, hydrogen and oxygen, i.e., the essential nuclear chemical structure is formed by these elements along. However, these oils may be substituted with other elements such as halogens, e.g., chlorine and fluorine. Some representative components of ester lubricants are ethyl palmitate, ethyl stearate, di(2-ethylhexyl) sebacate, ethylene glycol dilaurate, di(2-ethylhexyl) phthalate, di(1,3-methyl butyl) adipate, di-(2-ethyl butyl) adipate, di(1-ethyl propyl) adipate, diethyl oxylate, glycerol tri-n-octoate, di-cyclohexyl adipate, di-(undecyl) sebacate, tetraethylene glycol-di-(2-ethylene hexoate), di-Cellosolve phthalate, butyl phthaliyl butyl glycolate, di-n-hexyl fumarate polymer, dibenzyl sebacate, and diethylene glycol bis (2-n-butoxy ethyl carbonate). 2-ethylhexyl-adipate-neopentyl glycyl-adipate-2-ethylhexyl, is a representative complex ester. Generally, these synthetic ester lubricants have a viscosity ranging from light to heavy oils, e.g., about 50 SUS at 100° F. to 250 SUS at 210° F., and preferably 30 to 150 SUS at 210° F.

The esters are manufactured, in general, by mere reaction of the alcoholic and acidic constituents, although simple esters may be converted to longer chain components by transesterification. The constituents, in the proportions suitable for giving the desired ester, are reacted preferably in the presence of a catalyst and solvent or water entraining agent to insure maintenance of the liquid state during the reaction. Aromatic hydrocarbons such as xylene or toluene have proven satisfactory as solvents. The choice of solvent influences the choice of temperature at which the esterification is conducted; for instance, when toluene is used, a temperature

of 140° C. is recommended; with xylene, temperatures up to about 195° C. may be used. To provide a better reaction rate an acid esterification catalyst is often used. Many of these catalysts are known and include, for instance, HCl, H_2SO_4, $NaHSO_4$, aliphatic and aromatic sulfonic acids, phosphoric acid, hydrobromic acid, HF and dihydroxyfluoboric acid. Other catalysts are thionyl chloride, boron trifluoride and silicon tetrafluoride. Titanium esters also make valuable esterification and transesterification catalysts.

In a preferred reaction, about 0.5 to about 1 weight percent, or advantageously, 0.2 to 0.5% of the catalyst is used with xylene solvent at a tempertaure of 165 to 200° C. while refluxing water. The temperatures of the reaction must be sufficient to remove the water from the esterification mass as it is formed. This temperature is usually at least about 140° C. but not so high as to decompose the wanted product. The highest temperature needed for the reaction will probably be about 200° C., preferably not over about 175° C. The pressure is conveniently about atmospheric. Although reduced pressure or superatmospheric pressure could be utilized, there is usually no necessity to use reduced pressures, as the temperatures required at atmospheric pressure to remove the water formed do not usually unduly degrade the product.

When reacting glycols with dibasic acids to produce a polyester, it is preferred to continue the reaction with concomitant boiling off of water from the reaction mixture until the polyester product has a kinematic viscosity of about 15 to 200 centistokes at 210° F., preferably about 40 to 130 centistokes. When this point has been reached, the polymerization can be stopped, for instance, by adding a "capping alcohol" to the reaction mixture, and continuing to reflux until water ceases to be evolved. The capping alcohol is a low molecular weight monoalcohol of up to about 20 carbon atoms. It is standard practice, when esters are made using the conventional acid catalysts such as sodium bisulfate or paratoluenesulfonic acid to give the esters an after-treat by washing the ester with a 5 percent aqueous K_2CO_3 solution or by heating the ester in an autoclave for 15 hours at 340

TABLE I.—RESULTS OF OXYGEN ABSORPTION TESTS

[Conditions: 450° F.; 1 ft.[3] O_2/hr.; 75 g. fluid]

Run No.	Base fluid	Additives	Conc. (wt. percent)	Induction period (min.)	Total time (min.)	Volume of O_2 absorbed (ml.)
	Base oil A [1]	None		5	119	3,000
1	do	Phenothiazine	1.0	205	247	2,500
2	do	do	0.5	117	146	2,500
3	do	do	0.5			
		3-aminoquinoline	0.5		*563	2,500
4	do	Phenothiazine	0.5			
		3-aminoquinoline	0.5	84	147	2,500
		Iron octoate [2]	.083			
5	do	Phenothiazine	0.5			
		3-aminoquinoline	0.5			
		2,2'-dipyridylamine	1.0		*465	2,500
		Iron octoate	.083			
6	do	2,2'-dipyridylamine	2.0	9	35	1,056
7	do	3-aminoquinoline	1.0	10	82	2,500
8	do	do	2.0	114	134	1,320
9	do	Phenothiazine	0.5			
		2-aminopyridine	0.5	305	361	2,500
10	do	Phenothiazine	0.5			
		2-aminopyridine	0.5	195	245	2,500
		Iron octoate	.083			
11	do	Phenothiazine	0.5			
		2-aminopyridine	0.5			
		2,2'-dipyridylamine	1.0		*522	2,500
		Iron octoate	.083			
12	do	2-aminopyridine	2.0	15	31	660
13	do	Phenothiazine	1.0			
		2,2'-dipyridylamine	1.0		*593	2,500
14	do	Phenothiazine	1.0			
		2,2'-dipyridylamine	1.0		*572	2,500
		Iron octoate	.083			
139	Trimethylol-propane pelargonate.	Phenothiazine	.5			
		3-aminoquinoline	.5	318	354	2,500
283	do	Phenothiazine	.5			
		3-aminoquinoline	.5	301	335	2,500
		2,2'-dipyridylamine	1.0			
285	do	Phenothiazine	.5			
		3-aminoquinoline	.5			
		2,2'-dipyridylamine	1.0		*538	1,560
		Iron octoate	.083			
316	Oil B [3]	Phenothiazine	.5			
		3-aminoquinoline	.5		*474	1,190
		2,2'-dipyridylamine	1.0			
317	do	Phenothiazine	.5			
		3-aminoquinoline	.5			
		2,2'-dipyridylamine	1.0		*482	980
		Iron octoate	.083			
318	do	Phenothiazine	.5			
		2-aminopyridine	.5		*481	1,035
		2,2'-dipyridylamine	1.0			
319	do	Phenothiazine	.5			
		2-aminopyridine	.5			
		2,2'-dipyridylamine	1.0		*474	1,690
		Iron octoate	0.083			
1	Oil C [4]	Phenothiazine	0.2	216	248	2,500
2	do	do	0.5	311	352	2,500
3	do	do	0.2			
		2,2'-dipyridylamine	0.3	193	212	2,500
4	do	Phenothiazine	1.0	283	330	2,500
5	do	do	1.0			
		2,2'-dipyridylamine	1.0	338	365	2,500

[1] An ester from pentaerythritol and a mixture of aliphatic monocarboxylic acids with an average chain length of seven carbon atoms. Typical inspection data: Acid No. 0.01; sap. No. 400; K.V. at 210° F., 5.30 cs.; K.V. at 100° F., 28.4 cs.

[2] A concentrate of iron octoate in mineral oil containing 6.0% iron.

[3] An ester from trimethylolpropane and a mixture of valeric and pelargonic acids. Typical inspection data: Acid No. 0.03; sap. No. 372; K.V. at 10° F., 3.41 cs.; K.V. at 100° F., 14.4 cs.

*The test was stopped at this point. The end of the induction period had not been reached, however.

[4] Bis(2,2,4-trimethyl-pentyl) sebacate. It should be noted that Runs 3 to 5 with this oil were conducted in a different apparatus where the test is more severe for some unknown reason.

to 350° F. with 10 weight percent of propylene oxide. It is also conventional to subject the ester to filtration to remove insoluble materials. After this the product may be subjected to a reduced pressure distillation or stripping at 100° to 200° C. to remove volatile materials, such as water, the solvent and light ends.

Samples of ester fluids with and without phenothiazine and aminoquinoline or aminopyridine and samples made according to the present invention were subjected to oxygen absorption tests at 450° F. The tests were conducted by passing a stream of oxygen at the rate of one cubic foot per hour through 75 grams of the ester fluid containing the inhibitors and comparing the amount of oxygen absorbed vs. time. The induction period is the time in which little or no oxygen is absorbed by the fluid. The end of the induction period is signaled by a marked increase in the rate of oxygen absorption. The results of these tests are shown in Table I.

The data in Table I demonstrate the advantageous oxidation resistance provided by the addition of phenothiazine and dipyridylamine to synthetic ester fluids. The data also show the ability of the additives of the present invention in overcoming the adverse effects of iron salts on inhibitor life and to prevent oxygen up-take for a far longer period of time.

A synthetic ester fluid containing the inhibitor combination of the present invention was also subjected to the ERDCO–WADC Bearing Rig Head mounted on an ERDCO Universal Tester. For comparison a sample containing phenothiazine and aminoquinoline was also tested.

The test conditions and results are listed in Table II.

Conditions:

Duration	100 hours
Test bearing speed	10,000±100 r.p.m.
Test bearing load	500 radial
Test bearing temperature	500±10° F.
Test oil temperature	400±10° F.
Test oil sump temperature	440±5° F.
Test oil flow	600 ml./min.
Air flow	15,000 cc./min.

Results:

TABLE II.—RESULTS OF ERDCO-WADC HIGH TEMPERATURE BEARING RIG

Test No.	Base fluid	Additives	Conc. (wt. percent)	Initial K.V. at 100° F. (cs.)	Final K.V. at 100° F. (cs.)	Initial acid No.	Final acid No.
14	Oil A	Phenothiazine	.5	26.45	190.2	0.04	8.50
		3-aminoquinoline	.5				
15	do	Phenothiazine	.5	26.23	75.27	0.02	5.64
		3-aminoquinoline	.5				
		2,2'-dipyridylamine	1.0				

The change in viscosity and acid number of the fluid during a test is a measure of the effectiveness of the inhibitors. As the results show, the viscosity of the fluid containing dipyridylamine increases very little as compared to a fluid which did not contain the dipyridylamine.

Other examples of formulations within the present invention are as follows:

Example I

	Parts by wt.
Plexol–201 [1]	97.5
Glycol titanate polymer [2]	1.0
Phenothiazine	0.5
3-aminoquinoline or 2-aminopyridine	0.5
D.C.F. 200–60,000 [3]	0.001
2,2'-dipyridylamine	0.5

[1] A diethylhexyl sebacate oil having a kinematic viscosity at 100° F. of 12.3 cs., a viscosity index of 154, a pour point of below −80° F. and acid No. of 0.12.
[2] A polymer derived from tetrabutyl titanate and 2-ethyl-1,3-hexanediol.
[3] D.C.F. 200–60,000 is a methyl silicone polymer having a viscosity of 60,000 cs. at 25° C. and is an anti-foaming agent.

Example II

	Parts by wt.
Plexol–255 [1]	98.75
Phenothiazine	0.5
Glycol titanate polymer [2]	0.25
3-aminoquinoline or 2-aminopyridine	0.5
2,2'-dipyridylamine	1.0
Sebacic acid	.0075
D.C.F. 200–60,000	.001

[1] A mixture of diisooctyl adipate, di-tridecyl sebacate and Acryloid-966 (a copolymer of alkyl methacrylates and N-vinyl pyrolidone).
[2] See Example I.

Example III

	Parts by wt.
Diisooctyl azelate	25.5
Complex ester [1]	74.0
Phenothiazine	0.5
Free azelaic acid	0.01
3-aminoquinoline or 2-aminopyridine	0.5
2,2'-dipyridylamine	1.0
D.C.F. 200–60,000	0.001

[1] Derived from the reaction of one mole of neopentyl glycol, 2 moles of azelaic acid and two moles of isooctyl alcohol.

I claim:

1. A lubricant composition consisting essentially of an ester-based synthetic fluid of lubricating viscosity, about 0.01 to 5% by weight of phenothiazine and about 0.01 to 5% by weight of dipyridylamine and sufficient to retard oxidation of said ester based synthetic fluid at temperatures in excess of 400° F., said ester based fluid being an ester of an alkanol of 4 to 12 carbon atoms and an alkane carboxylic acid of 4 to 12 carbon atoms.

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

3. The lubricant composition of claim 2 to which is added about 0.3 to 5% by weight of a material selected from the group consisting of aminoquinoline and aminopyridine.

4. The lubricant composition of claim 3 containing about 0.3 to 2% by weight of 2,2'-dipyridylamine, about 0.3 to 2% by weight of phenothiazine and about 0.3 to 2% by weight of 3-aminoquinoline.

5. A lubricant composition consisting essentially of an ester-based synthetic fluid of lubricating viscosity, about 0.01 to 5% by weight of phenothiazine, about 0.01 to 5% by weight of dipyridylamine and sufficient to retard oxidation of said ester-based synthetic fluid at temperatures in excess of 400° F., said ester-based fluid being an ester of an alkanol of 4 to 12 carbon atoms and an alkane carboxylic acid of 4 to 12 carbon atoms which ester has terminal monohydric alcohol residues containing at least one hydrogen atom on the beta carbon atom.

6. A lubricant composition consisting essentially of an ester-based synthetic fluid of lubricating viscosity, about 0.3 to 2 weight percent of phenothiazine, about 0.3 to 2 percent of 2-aminopyridine and about 0.3 to 2 weight percent of 2,2'-dipyridylamine, said ester-based fluid being an ester of an alcohol of 4 to 12 carbon atoms and an alkane carboxylic acid of 4 to 12 carbon atoms.

7. The lubricant composition of claim 6 in which the ester has terminal monohydric alcohol residues containing at least one hydrogen atom on the beta carbon atom.

8. The lubricant composition of claim 1 to which is

added about 0.1 to 5% by weight of a material selected from the group consisting of aminoquinoline and aminopyridine.

9. The lubricant composition of claim 8 in which the ester has terminal monohydric alcohol resides containing at least one hydrogen atom on the beta carbon atom.

10. The composition of claim 8 wherein the dipyridylamine is 2,2'-dipyridylamine.

References Cited by the Examiner

UNITED STATES PATENTS

2,136,788	11/1938	Fairlie	252—401
2,198,961	4/1940	Dietrich	252—401
2,318,196	5/1943	Chenicek	252—401
2,948,680	8/1960	Fields	44—63
2,961,406	11/1960	McNeil	252—56
3,038,858	6/1962	Verley	252—47
3,048,542	8/1962	Tierney et al.	252—47.5
3,078,230	2/1963	Cyba	252—401

FOREIGN PATENTS

786,767	11/1957	Great Britain.

OTHER REFERENCES

Atkins et al., "Development of Additives and Lubricating Oil Compositions," I. and E. Chem. 39, 491–493 (No. 4, April 1947).

Cole et al.: "Survey of the Literature on Antioxidants and Anticorrosion Additives for Lubricants at Elevated Temperatures," WADC Technical Report 53–353 (1954), Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, page 62 pertinent.

DANIEL E. WYMAN, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*