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LUBRICANT COMPOSITION

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This invention relates to ester based lubricant compositions containing a novel combination of base oil-soluble additive agents.

Organic compounds such as lubricant 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. These synthetic fluids are not sufficiently resistant to oxidation to be useful alone. They can, however, be adequately protected by use of small amounts of additives. N-phenyl-1-naphthylamine has been employed extensively to protect synthetic fluids against oxidation. Its activity, however, is not great enough to protect fluids for long periods of time above about 400° F.

It is the particular object of the present invention to provide an ester oil of lubricating viscosity that exhibits increased resistance to oxidation under high temperatures such as in excess of 400° F. Further, the additives of the present invention have proven far more effective than the conventional use of N-phenyl-1-naphthylamine alone in reducing oxidation in synthetic ester fluids.

The present invention provides an improved ester-based lubricant composition containing N-phenyl-1-naphthylamine and a component selected from the group of dipyridylamine, aminoquinoline, aminopyridine and mixtures thereof in minor amounts effective to impart to the lubricant increased resistance to oxidation. The amounts added should be soluble in the base oil into which they are introduced and these amounts will vary with the particular base oil utilized.

The preferred aminoquinolines which are used in the present invention are 3-aminoquinoline and 8-aminoquinoline and their ring-substituted derivative e.g. alkyl-substituted. Among the useful aminopyridines are 2-aminopyridine and the ring-substituted, e.g., alkyl-substituted aminopyridines. The dipyridylamine additive useful in the present invention can be ring-substituted, as for example, with alkyl groups, the preferred dipyridylamine being 2,2'-dipyridylamine. Each of the aminoquinoline, aminopyridine and dipyridylamine or their mixture may be added in amounts from about .01 to 5 percent by weight of the final composition with a

preferred amount of from about 0.1 to 2 percent by weight of the final composition. These additives are normally added to the ester-based lubricant along with the N-phenyl-1-naphthylamine. The N-phenyl-1-naphthyl amine is usually present in amounts from about .01 to 5 percent by weight of the final composition with a preferred amount being from about 0.1 to 2 percent and the N-phenyl-1-naphthylamine may be substituted as with alkyl groups, for instance, in the napthyl or phenyl ring. For best results the relative concentrations of the additives will vary with the particular ester lubricant employed and will also be dependent on the characteristics of the final lubricant composition desired. Normally, it is preferred that the dipyridylamine, aminoquinoline or aminopyridine to N-phenyl-1-naphthylamine weight ratio be about 0.5 to 2:1, advantageously about 0.75 to 1.5:1. Increasing the amounts of dipyridylamine, aminoquinoline or aminopyridine will generally be beneficial.

The lubricant composition of this invention includes as the major compound 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 poly-hydroxy aliphatic alcohols and aliphatic carboxylic acids, frequently of about 4 to 12 carbon atoms; aliphatic including cycloaliphatic. 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 the reaction product of 1 mole of a dicarboxylic acid, say of 6 to 10 carbon atoms, with 2 moles of a monohydric alcohol or of 1 mole of a glycol of 4 to 10 carbon atoms with two moles of a monocarboxylic 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 polyesterifiaction 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. The acryloids are polymers of mixed C_4 to C_{18} polymers 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. 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. If the alcohol has no hydrogens on the beta carbon atoms, it is neo-structured; and esters of such alcohols are often preferred. In particular, the neo-C_8 alcohol—2,2,4-trimethyl-pentanol-1—gives lubricating diesters or complex esters suitable for blending with diesters to produce lubricants which meet stringent viscosity requirements. Iso-octanol and iso-decanol are alcohol mixtures made by the oxo process from C_3–C_4 copolymer heptanes. The cut which makes up iso-octanol usually contains about 17% 3,4-dimethylhexanol; 29% 3,5-dimethylhexanol; 23% 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-hexanediol, 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, ether glycols may be used, for instance, where the alkylene radical contains 2 to 4 carbon atoms such as diethylene glycol, dipropylene glycol and ether 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 tetra hydroxy aliphatic alcohols having about 4 to 12 carbon atoms, preferably about 5 to 8 carbon atoms; for instance pentaerythritol, trimethylolpropane 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 "isosebacic" 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 United States Patents 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 alone. 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), dicellosolve phthalate, butyl phthallyl 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 a xylene solvent at a temperature 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 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 without N-phenyl-1-naphthylamine and dipyridylamine, aminoquinoline or aminopyridine and samples made according to the present invention in various ester-based fluids were subjected to the oxygen absorption tests. The tests were conducted at 450° F. 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 signalled by a marked increase in the rate of oxygen absorption. The results of these tests are shown in Table I.

The length of the induction period serves as a significant measure of the relative effectiveness of the inhibitors. As shown in Table I, addition of the novel additive combination of the present invention protects the fluid against rapid oxidation for a longer period of time than would be expected.

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

EXAMPLE I

	Parts by weight
Plexol-201 [1]	98.0
Titanium polymer [2]	1.0
N-phenyl-1-naphthylamine	0.5
2,2'-dipyridylamine	0.5
D.C.F. 200–60,000 [3]	0.001

[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 weight
Plexol-255 [1]	99.25
Glycol titanate polymer [2]	0.25
N-phenyl-1-naphthylamine	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 pyrrolidone).
[2] Polymer derived from titanium tetra-alkyl esters and glycol.

EXAMPLE III

	Parts by weight
Diisooctyl azelate	26.0
Complex ester [1]	74.0
Free azelaic acid	0.01
N-phenyl-1-naphthylamine	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.

In the compositions of Examples I, II and III, the 2,2'-dipyridylamine can be replaced with similar parts by weight of 2-aminopyridine or 3-aminoquinoline and obtain essentially similar results. Also, in Table I, 2,2'-dipyridylamine and 2-aminopyridine can be replaced with 1.0 parts by weight of 3-aminoquinoline and obtain essentially similar results.

TABLE I

Results of Oxygen Absorption Tests

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

Run No.	Base Ester	Additives	Conc. (Wt. %)	Induction Period (min.)
80	Oil A[1]	None		5
330	do[1]	N-Phenyl-1-naphthylamine	1.0	97
331	do[1]	do	1.0	305
		2,2'-Dipyridylamine	1.0	
379	do[1]	do	1.0	10
380	Oil B[2] 6.3	N-Phenyl-1-naphthlyamine	1.0	130
383	do	do	1.0	[3] 367
		2,2'-Dipyridylamine	1.0	
386	Celanese 304[4]	N-Phenyl-1-naphthylamine	1.0	82
388	do[1]	do	1.0	299
		2,2'-Dipyridylamine	1.0	
400	Oil A[1]	N-Phenyl-1-napthylamine	1.0	276
		2-Aminopyridine	1.0	
306	Trimethylolpropane tripelargonate.	do	1.5	13
46	Neo-octylsebacate	do	0.3	10

[1] An ester from pentaerythritol and a mixture of aliphatic monocarboxylic acids with an average chain length of seven carbons. Typical inspection data: acid No., 0.01; sap. No., 400; K.V. @ 210° F., 4.95 cs.; K.V. 100° F., 26.37 cs.
[2] An ester prepared from trimethylolpropane and a 70-30 wt. percent mixture of caproic and n-heptanoic acids.
[3] Test stopped. Induction period not yet ended.
[4] An ester from trimethylolpropane and n-heptanoic acid. Typical inspection data; acid No., 0.03; sap. No., 350; K.V. @ 210° F., 3.46 cs.; K.V. @ 100° F., 14.82 cs.

It is claimed:

1. A lubricant composition consisting essentially of a major amount of synthetic ester of lubricating viscosity and minor amounts effective to retard oxidation, of N-phenyl-1-naphthylamine and a material selected from the group consisting of dipyridylamine, aminoquinoline and aminopyridine, said ester-based fluid being of an alkanol of 4 to 12 carbon atoms, said minor amounts being about 0.01 to 5 percent by weight, and an alkane carboxylic acid of 4 to 12 carbon atoms.

2. The composition of claim 1 which contains 2,2'-dipyridylamine.

3. The composition of claim 1 which contains 2-aminopyridine.

4. The composition of claim 1 which contains 3-aminoquinoline.

5. The lubricant composition of claim 2 containing about 0.1 to 2 percent by weight of 2,2'-dipyridylamine and about 0.1 to 2 percent by weight of N-phenyl-1-naphthylamine.

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UNITED STATES PATENTS

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2,318,196	Chenicek	May 4, 1943
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Cohen et al.: "I. and E. Chem.," volume 45, No. 8, August 1953, page 1767 pertinent.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Daniel B. Eickemeyer

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 3, after "ester" insert -- fluid --; lines 8 and 9, strike out ", said minor amounts being about 0.01 to 5 percent by weight,"; line 10, after "atoms" insert -- said minor amounts being about 0.01 to 5 percent by weight --.

Signed and sealed this 23rd day of March 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

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Commissioner of Patents

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