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3,038,858

ESTER BASED LUBRICANT COMPOSITION CONTAINING PHENOTHIAZINE AND AMINOPYRIDINE

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This invention relates to ester-based lubricant compositions and more particularly to ester-based lubricant compositions containing phenothiazine and aminopyridine which are effective as corrosion inhibitors or antioxidants.

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 into 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. Numerous oxidation and corrosion inhibitors have been found for use in lubricating compositions and many combinations thereof also have been tested. In many instances the effect of such combination is merely the effect of each of the inhibitors employed, but in other cases a greater effect is exhibited by the additives used, thus promoting to an unaccountable degree the oxidation and corrosion protection of the composition.

It is the particular object of the invention to provide an ester oil of lubricating viscosity having the superior lubricant properties characteristic of the synthetic ester oils, and inhibited with respect to oxidation deterioration. Further, the additives of this invention have proven to be effective in retarding sludge formation in synthetic ester lubricants which are exposed to high temperatures, and also have proven far more effective than the conventional use of phenothiazine alone in retarding sludge formation in ester fluids made from a branched "neo-" structured alcohol component.

The present invention provides an improved ester-based lubricant composition containing phenothiazine and aminopyridine so as to exhibit increased resistance to oxidation under high temperatures such as in excess of 400° F.

The preferred amines utilized in this invention are 2-aminopyridine, 2,6-diaminopyridine, 4-methyl-2-aminopyridine and their substituted derivatives. The aminopyridine may be added in amounts from about .01 to 5 percent by weight of final composition with a preferred amount of from about .1 to 2 percent by weight of final composition. The additive selected from this group is normally added to the ester-based lubricant along with the phenothiazine. The phenothiazine is normally present in amounts from about .01 to 5 percent by weight of final composition with a preferred amount being from about .1 to 2 percent, and the phenothiazine may be substituted as with alkyl groups. The relative concentrations of the additives will vary with the particular ester lubricant employed and also dependent upon the characteristics of the final lubricant composition desired. Normally, it is preferred that the amine to phenothiazine ratio should be greater than about 1 to 1.

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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 grouping such as in complex esters, polyesters or diesters. These esters are made from mono- and polyfunctional aliphatic alcohols and aliphatic carboxylic acids, frequently of about 4 to 12 carbon atoms. The reaction product of a mono-functional 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 of, for instance 6 to 12 carbon atoms 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. A complex ester is usually considered to be of the type $X-Y-Z-Y-X$ in which X represents a monoalcohol 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. 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_3 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. In particular, the neo- C_8 alcohol—2,2,4-trimethyl-pentanol-1—gives 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 heptenes. The cut which makes up iso-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-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-dimethyl-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. pentaerythritol, trimethylol propane and the like.

Preferred monocarboxylic acids are those of 8 to 24 carbon atoms such as stearic, lauric, etc. The dicarboxylic acids employed in making ester lubricants will in general contain from about 4 to 12 carbon atoms. Suitable acids are described in U.S. 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 dicarboxylic acids containing not more than about 12 carbon atoms, and mixtures of these acids. Such acids include succinic, adipic, suberic, azelaic, and sebacic 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 di-laurate, di-(2-ethylhexyl) phthalate, di-(1,3-methylbutyl) adipate, di(2-ethylbutyl) adipate, di(1-ethylpropyl) adipate, diethyl oxylate, glycerol tri-n-octate, di-cyclohexyl adipate, di-(undecyl) sebacate, tetraethylene glycol di-(2-ethylene hexoate), di-Cellosolve phthalate, butyl phthalyl butyl glycolate, di-n-hexyl fumarate polymer, dibenzyl sebacate, and diethylene glycol bis(2-n-butoxy ethyl carbonate). 2-ethylhexyl-adipate-neopentyl glycol 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 dihydroxyfluoroboric 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 mono-alcohol 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 paratoluene-sulfonic 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 an oxidation inhibitor

and samples containing aminopyridine alone, phenothiazine alone and samples made according to the present invention containing varying portions of aminopyridine and phenothiazine are compared in a modified MIL-L-9236 corrosion-oxidation tests run at 450° F. for a period of about 20 hours. The test was conducted by passing a stream of air at the rate of 5 liters per hour through 100 ml. of the sample and one inch square coupons of copper, steel and magnesium. Oil insolubles were determined by centrifuging the fluid upon completion of the test. Acid number, viscosity and pentane insolubles were determined on the centrifuged oil. Percent "total insolubles" represents the sum of the oil insolubles and pentane insolubles. Results are shown in Table I.

I claim:

1. A lubricant composition consisting essentially of an ester-based fluid of lubricating viscosity, about 0.01 to 5% by weight phenothiazine and about 0.01 to 5% by weight aminopyridine and effective to retard oxidation of said ester-based fluid at temperatures in excess of 400° F., said ester-based fluid being of an ester of an alcohol of 4 to 12 carbon atoms and a carboxylic acid of 4 to 12 carbon atoms.
2. The lubricant composition of claim 1 where aminopyridine is 2-aminopyridine.
3. The lubricant composition of claim 1 wherein the alcohol and carboxylic acid of 4 to 12 carbon atoms are aliphatic.

Table I

Base Fluid.....	Neopentylidodecanate				Bis(2,2,4-trimethylpentyl) sebacate								Lubricant A ¹		
Additives (Wt. Percent)															
Phenothiazine.....	0.5		0.3		0.5		0.2		0.2		0.2		0.5	0.5	0.5
2-Aminopyridine.....		0.5	0.2			0.5	0.3								
4-Methyl-2-aminopyridine.....								0.5	0.3						
2,6-Diaminopyridine.....									0.5	0.3					
Run No. 800.....	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Acid No. Rise.....	23.6	10.5	9.85	5.94	6.96	9.19	9.4	8.16	11.2	8.90	7.8	11.0	15.0	7.48	2.30
Percent Vis. Change.....	134.0	5.0	21.0	-3.0	64.0	25.0	11.5	9.4	13.0	20.4	25.5	18.1	85.4	58.0	20.2
Percent Oil Insolubles.....	.12	2.5	4.0	4.5	8.0	2.0	2.8	2.5	3.0	3.8	7.5	5.0	trace	trace	.6
Percent total Insolubles.....	2.0	4.0	9.0	8.0	10.0	3.5	5.0	3.5	5.0	7.2	9.0	7.5	trace	3.0	3.0
Metals Corrosion, mg./cm. ² :															
Mg.....	-41.8	-16	-34.8	-19.9	-42.2	.01	-1.04	-.09	-1.28	-15.3	-21.2	-2.83	0.25	2.33	-0.8
Cu.....	-.08	-.83	.16	.27	-.61	-1.47	-.02	.04	0.00	-.06	.11	.02	-6.94	-1.06	.06
St.....	-.02	.09	.18	.17	-.32	.09	.14	.10	-.14	.08	.13	.06	.02	.08	.12

¹ n-C₇-acid-pentaerythritol ester having the following inspection data: Acid No. 0.01, Sap. No. 400, vis. at 210° F., 5.30 cs.; vis. at 100° F., 23.4 cs.

Further evidence of the advantages to be obtained by using a composition of this invention are shown in the results of oxygen-adsorption 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 adsorbed vs. time. The induction period is the time in which little or no oxygen is adsorbed by the fluid. The end of the induction period is signalled by a marked increase in the rate of oxygen adsorption. The results of these tests are shown in Table II.

Table II

Base Fluid	Additive	Conc. (Wt. percent)	Induction Period (min.)
Bis(2,2,4-trimethylpentyl) sebacate.	None.....		8.6
Do.....	Phenothiazine.....	.2	183.0
Do.....	2-Aminopyridine.....	.3	10.5
Do.....	Phenothiazine 2-Aminopyridine.....	.2	426.0
Do.....	Phenothiazine.....	.3	
Do.....	Phenothiazine.....	.1	117.0
Lubricant ¹	None.....		5.0
Do ¹	Phenothiazine.....	.5	117.1
Do ¹	Phenothiazine 2-Aminopyridine.....	.5	336.8

¹ See Table I.

The induction period serves as a significant measure of the relative effectiveness of the inhibitors. As shown in Table II, the 2-aminopyridine-phenothiazine synthetic ester-based lubricant composition prevents oxygen uptake by the fluid by more than twice as long as does phenothiazine alone and also more than twice as long as would be expected from the results obtained when using aminopyridine and phenothiazine alone.

4. The lubricant composition of claim 2 containing about 0.1 to 2 percent by weight of phenothiazine.
5. The lubricant composition of claim 4 containing about 0.1 to 2 percent by weight of 2-aminopyridine.
6. The lubricant composition of claim 3 wherein the carboxylic acid of 4 to 12 carbon atoms is selected from the group consisting of aliphatic monocarboxylic acids and aliphatic dicarboxylic acids.
7. The lubricant composition of claim 6 wherein the aliphatic alcohol of 4 to 12 carbon atoms has no hydrogen on a beta carbon atom.
8. The lubricant composition of claim 6 wherein the ratio of aminopyridine to phenothiazine is greater than about 1:1.
9. The lubricant composition of claim 6 wherein the aliphatic alcohol of 4 to 12 carbon atoms has no hydrogen on a beta carbon atom and the ratio of aminopyridine to phenothiazine is greater than about 1:1.
10. The lubricant composition of claim 9 wherein the aminopyridine is 2-aminopyridine.

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