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LUBRICANT CONTAINING A FATTY ACID AMIDE OF PHENOTHIAZINE

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This invention is concerned with oleaginous base lubricants having exceptional oxidation resistance at high temperatures. The compositions contain a base oil of lubricating viscosity and a small amount of a fatty amide of phenothiazine.

Mineral oil and synthetic ester lubricants, in the form of greases or free-flowing liquids are called upon to ease friction and prevent damage to machinery operated at temperatures up to as high as about 450° F. At these higher temperatures, the internal combustion engine is an ideal oxidizing machine, since the motor oil is violently agitated in the presence of air for lengthy periods of time. Greases are subject to similar conditions in their many applications.

Over the range of temperatures developed when employing lubricants, the rate of oil and grease oxidation approximately doubles for each 20° F. rise of temperature Thus oil exposed to aeration at 300° F. may oxidize at a rate about 32 times as great as at 200° F. While well refined motor oils will oxidize to only a negligible extent at temperatures of the order of 200° F. and lower, oxidation may become quite pronounced at temperatures of 250° F. and higher. In addition, metals act as powerful oxidation catalysts or accelerators, iron, copper and lead being particularly active. The rate of motor oil oxidation may accordingly be increased as much as 100-fold, at any given temperature, due to exposure to engine metal surfaces, metal particles resulting from normal engine wear, and contamination with combustion chamber blow-by solids and air-borne dust.

All the various types of hydrocarbon constituents of lubricating oils and greases are susceptible to oxidation, if exposed to sufficient air or oxygen and at sufficiently elevated temperatures. Paraffinic hydrocarbons, both straight- and branched-chain, and naphthenic hydrocarbons are readily reactive. Aromatic hydrocarbons, other than some naphthalene and anthracene derivatives, are indicated to be even more susceptible, possibly because of the activating influence of the aromatic ring structure. Synthetic ester lubricants are basically paraffinic in structure differing from hydrocarbon lubricants in many instances by the insertion of ether oxygen atoms in the chain and the partial oxidation of some carbon atoms.

Of even more importance from an engine performance viewpoint are the oxidation end-products formed. Probably one of the first types of oxidation products formed in an oil undergoing oxidation is organic peroxides, which may act as catalysts, causing oxidation of additional components in an oil, or more intensive oxidation of slightly oxidized constituents. Peroxides have also been indicated to be vigorously corrosive to sensitive types of engine bearings. One of the chief ends-products of the oxidation of paraffin hydrocarbons is organic acids, ranging from formic and acetic up to high molecular weight fatty acids. Alcohols, aldehydes, and ketones also appear to be produced, while more drastic oxidation of paraffin hydrocarbons may yield oxy or hydroxy acids, esters, lactones and complex condensation products of high molecular weight. The acids formed by paraffin oxidation, particularly those of low molecular weight, are vigorously corrosive to copper-lead and cadmium engine bearings. The more complex oxy-acids have

been indicated to be a cause of piston ring sticking. Naphthenic hydrocarbons probably oxidize and yield oxy-products in a manner very similar to the paraffins.

The aromatic hydrocarbon constituents of lubricating oils tend to be the most readily oxidized, possibly because of the sensitivity of the hydrogen atoms in side chains adjacent to the aromatic ring nucleus, yielding acids and acidic oxy-products of the same general types as the paraffins. Subsequent oxidation of the aromatic ring residue probably results in formation of very complex condensation and polymerization products which tend to be oil-insoluble. These types of oxidation products probably constitute the sludges, resins and varnishes which are formed by the oxidation of the more asphaltic or aromatic types of mineral oils. Thus, highly refined, paraffinic oils of high viscosity index tend to become acidic and corrosive to bearings, but do not form excessive oxidation sludges or varnishes in severe engine service, whereas oils of lower V.I. and containing considerable aromatic constituents tend to develop excessive engine sludges and varnishes.

As is well known, commercial lubricating compositions generally contain an oxidation inhibitor. The exact mechanisms by which inhibitors minimize or retard oil oxidation are not known, although it is probable that they function by decomposing organic peroxides as they are formed so that their catalytic effect is nullified. Similarly, inhibitors probably tend to "poison" or counteract metallic catalysts. Inhibitor additives do not eliminate or entirely prevent oxidation of the oleaginous lubricant when conditions of exposure are severe, and some types of oils are stabilized and improved to a much greater degree by inhibitors than are others. A satisfactorily stable and oxidation resistant oil requires careful refining of the base stocks plus proper selection of the type and concentration of inhibitor most suited to the particular oil.

The art has recognized several types of inhibitors. Elemental sulfur in small amounts can be dissolved in lubricating oils and is quite effective as an oxidation inhibitor. In order to render sulfur less corrosive to copper and still retain its inhibiting effect, it may be reacted with unsaturated fatty oils such as sperm oil or synthetic unsaturated fatty esters of similar general composition. Aromatic and aliphatic sulfides represent another type of compound sometimes utilized as an oxidation and corrosion inhibitor. Relatively simple sulfur-containing aromatics such as dibenzyl sulfide, dixylyl disulfide or dicetyl sulfide are sometimes utilized. More complex compounds of similar type are the alkyl phenol sulfides.

The effectiveness of phosphorus as an oxidation inhibitor in oils has been recognized for many years. Oil-soluble organic compounds of phosphorus such as alkyl and aryl phosphites, e.g., tributyl phosphite and triphenyl phosphite, and aluminum, calcium or barium salts of alkyl phosphoric acids are types of phosphorus compounds which display antioxidant properties. Inhibitors containing both sulfur and phosphorus are usually more effective and efficient in a wider variety of lube oil base stocks than those containing only phosphorus or sulfur, and many of the inhibited motor oils now on the market contain one kind or another of these combination sulfur-phosphorus type additives. One widely used type of sulfur-phosphorus additive is the dithiophosphates, which are prepared by the reaction of phosphorus pentasulfide with alcohols.

Oil-soluble organic amines and phenol derivatives, such as phenyl-α-naphthylamine and β-naphthol, have been used for many years as oxidation inhibitors in highly refined turbine oils, lubricating greases and the like. How-

ever, compounds of this type display but limited effectiveness in motor oils under the oxidizing conditions encountered in engines. It has been theorized that these simpler amines and phenols are essentially low temperature inhibitors, and as such are effective only at temperatures below about 200 or 250° F., which is considerably below those to which motor oils are exposed in engines operating at heavy loads. More complex amines and phenol derivatives such as tetramethyl diamino diphenylmethane and alizarin are used to some extent as motor oil inhibitors. However, these compounds are rarely used alone, but are applied in conjunction with other types of inhibitors, so that they may be considered more as supplemental additives rather than as primary inhibitors.

It has now been found that acid amides—in particular, fatty acid amides—of phenothiazine are superior agents to inhibit oxidation of oleaginous base lubricants in a temperature range of about 300 to 450° F. The compositions of this invention incorporate a small amount, sufficient to inhibit oxidation, of an acid amide of phenothiazine in the lubricating oil base which is the major portion of the composition. This inhibitor is preferably used in combination with low-temperature antioxidants, such as "Ortholeum 300" (a diphenylamine type) or zinc dithiophosphate which are effective below about 300° F., to provide a lubricant resistant to oxidation over the whole temperature range in which it will be used. The acid amide of phenothiazine frequently comprises about 0.1 to 5% of the final lubricant composition, preferably less than about 2%. The compositions of this invention have oxidation stability in a higher temperature range than oleaginous lubricants containing the amines mentioned above. For example, the fatty acid amides of phenothiazine in mineral oil effectively inhibited the oil to oxidation in an oxygen absorption test at 360° F. using copper and lead catalysts. Phenothiazine itself is ineffective an an additive for mineral oil based lubricants. It is only about 0.1% soluble in mineral oil. Attempts to solubilize 0.5%, by incorporating lauric acid in the base oil and heating the mixture, failed.

The novel additives of this invention are di-substituted amides formed easily by the reaction of a fatty acid with phenothiazine with the release of water. The additive may be made from fatty acids frequently having 10 to 20 carbon atoms. The length of the carbon atom chain is unimportant so far as the effect of the additive is concerned but it should be long enough to impart oil-compatible, i.e. soluble, dispersible or miscible, properties to the final amide. A length of over 32 carbon atoms has not been seen to impart any advantages. The amides may be used in mineral oil liquid lubricants, mineral oil based greases and synthetic greases. Naturally occurring fatty acids such as lauric and stearic acids are cheap and suitable for conversion to the additive. Synthetic monocarboxylic acids such as isodecanoic may be used with satisfactory effects. The reaction can be performed by heating roughly stoichiometric quantities of the ingredients, preferably in the presence of a water entraining agent such as toluene or xylene, in a temperature range of about 150° to 350° C. with a catalyst such as boric acid or boron trioxide. The reaction mass is kept agitated and heated until water ceases to be given off. A slight excess of phenothiazine may be used in the reaction, and the unreacted phenothiazine need not be removed from the product, since the phenothiazine amide has a solubilizing effect on the phenothiazine.

The mineral oil base stock used in the present invention is of lubricating viscosity and can be for instance a solvent extracted or solvent refined oil obtained in accordance with conventional methods of solvent refining lubricating oils. Generally, lubricating oils have viscosities from about 20 to 250 SUS at 210° F. The base oil may be derived from paraffinic, naphthenic, asphaltic or mixed base crudes, and if desired, a blend of solvent-treated Mid-Continent neutrals and Mid-Continent bright stocks may be employed. A particularly suitable base oil used in the preparation of the compositions described hereinafter is a solvent treated Mid-Continent neutral having a viscosity index of about 95.

Grease compositions may be prepared by the incorporation or formation in the oleaginous base of grease-thickening fatty acid soaps of metals such as the alkaline metals of groups I and II of the periodic table. The soap content of the grease is generally about 2–25%. Although the use of high viscosity oils (above 100 SUS at 100° F.) gives harder greases, the use of a low viscosity non-naphthenic 100 percent solvent refined neutral Mid-Continent base lubricating oil provides a grease having better low temperature pumpability. The soaps are usually the alkali metal or alkaline earth metal, e.g. lithium, barium, calcium, etc. salts of natural or synthetic long-chain carboxylic acids, such as stearic, hydroxy stearic or lauric acids say of 12 to 20 carbon atoms.

Greases which comprise about 2–25% of the above-mentioned soaps in a synthetic oleaginous base may also be given resistance to oxidation in the 300–450° F. temperature range by the use of acid amides of phenothiazine. One type of synthetic oleaginous base used is the ester synthetic oils of lubricating viscosity which consist essentially of carbon, hydrogen and oxygen. Various of these lubricating materials have been described in the literature and generally their viscosity ranges from the 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. These esters are of improved thermal stability, low acid number, and high flash and fire points. These complex esters, diesters, monoesters and polyesters may be used alone or, to achieve the most desirable viscosity characteritics, complex esters, diesters and polyesters may be blended with each other or with naturally occurring esters like castor oil to produce lubricating compositions of wide viscosity ranges which can be "tailor-made" to meet various specifications. This blending is performed, for example, 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.

These esters are prepared fundamentally by the action of acids on alcohols. The mere mixture of an alcohol and acid at the proper temperature will react to produce an equilibrium mixture which includes the monoester. The same is true for the reactions of organic dibasic acids and glycols to produce synthetic lubricant polyester bright stocks. The diesters are frequently of the type alcohol-dicarboxylic acid-alcohol, while complex esters are generally of the type X—Y—Z—Y—X in which X represents a mono-alcohol residue, Y represents a dicarboxylic acid residue and Z represents a glycol residue and the linkages are ester linkages. These esters 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. Greases which use these esters as the oleaginous base also have most of these characteristics.

Suitable mono and dicarboxylic acids used to make synthetic ester lubricant bases can be branched or straight chain and saturated or unsaturated and they contain from about 2 to 12 carbon atoms. The preferred acids are the saturated aliphatic dibasic acids which include, among others, succinic, adipic, diglycolic, suberic, azelaic, sebacic and "isosebacic" acids, which are mixtures of alpha-ethyl suberic acid, alpha-alpha'-diethyl adipic acid, and sebacic acid. The alcohols contain from 4 to 12 carbon atoms. The monohydric alcohols include, among others, butyl, hexyl, 2-ethylhexyl, dodecyl, cetyl and stearyl alcohols. The glycols and glycol ethers include eth-

ylene glycol, propylene glycol, butylene glycol, triethylene glycol, diethylene glycol, ethylene glycol mono-2-ethylhexyl ether, diethylene glycol mono-n-butyl ether, propylene glycol mono-n-butyl ether, tripropylene glycol mono-ethyl ether, 2-ethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 2-isopropyl-1,3-hexanediol, etc. In general the useful glycols include the aliphatic monoglycols of 4 to 20 or 30 carbon atoms, preferably 4 to 12, and the polyglycols having from about 1 to 50 ether oxygen atoms obtained from monoglycols of 2 to 12 carbon atoms. Advantageously, the polyglycols contain from about 1 to 10 ether oxygen atoms and these can be of the formula $H(OC_xH_{2x})_nOH$ where x is 2 to 4. The preferred polyglycols are the polyethylene and polypropylene glycols and those particularly useful have molecular weights from about 150 to 450.

Di-2-ethylhexyl sebacate (Plexol 201) and diisooctyl azelate (DiOAz) are preferred synthetic lubricant bases from the standpoint of economy, availability and satisfactory properties. DiOAz is a product made by the esterification of azelaic acid with an alcohol mixture made by the oxo process from C_3 to C_4 copolymer heptanes. This alcohol is commercially available as a mixture containing 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% alpha-alkyl alkanols and 5% other materials. Some other specific satisfactory diesters are di-(1,3-methylbutyl) adipate, di-(2-ethylbutyl) adipate, di-(1-ethylpropyl) adipate, diethyl oxalate and di-(undecyl) sebacate.

Materials normally incorporated in lube oils and greases to impart special characteristics can be added to the compositions of this invention. These include corrosion inhibitors, extreme pressure agents, antiwear agents, etc. The amount of additives included in the composition usually ranges from about 0.01 weight percent up to about 10 weight percent, and in general can be employed in any amounts desired so long as the composition is not unduly deleteriously affected.

The following examples give illustrative procedures for making phenothiazine amides.

EXAMPLE I

To a 3 liter round-bottom 4-necked flask equipped with an electric motor driven stirrer, water cooled reflux condenser, thermometer, water trap and heating mantle, were charged the following: 219 g. (1.1 moles) phenothiazine, (N.F. grade), 200 g. (1 mole) lauric acid (Eastman Kodak Co. red label grade) and 100 g. of commercial xylene. The mixture was heated to reflux at 193° C. over ½ hour and 57 g. xylene were removed in order to increase the reflux temperature. It was then refluxed at 255° C. Heating was continued for 20.5 hours dropping xylene and water during this time, and raising the reflux temperature to 295° C. A total of 15.5 cc. of water were removed. The mass was then blown with nitrogen at 250° C. until no odor of xylene could be detected. The dark brown product weighed 394 g. (sample 78). Some of this product was purified by dissolving it in 3 parts of hot hexane, cooling to room temperature and filtering it. This gave sample 80.

EXAMPLE II

The stearic acid amide of phenothiazine, was prepared as follows. To the same equipment described in the lauric acid run above, were charged 299 g. (1.5 moles) phenothiazine (N.F. grade), 284 g. (1 mole) stearic acid (Armour & Co. Neo Fat 1-65), 150 g. commercial xylene and 6 g. boron trioxide. The mixture was heated at reflux-173° to 190° C. for 20.5 hours dropping water and some xylene during this time. Then 4 g. more of boron trioxide were added and the mixture was refluxed for an additional 12.75 hours. A total of 18 cc. of water were obtained. The mass was then blown with nitrogen for 15 minutes at 265° C. to remove the xylene. The product (sample 105) weighed 552 g. Part of the product was treated with 8 times its weight of hot hexane. It was cooled to room temperature and filtered. The filtrate was evaporated to dryness to give sample 106. The hexane insoluble portion was treated with hexane again to give an extract, sample 107.

Properties of the phenothiazine amides are reported in Table I.

Table I

Acid Used	Sample No.	Saponification No.		Acid No.	Percent Yield
		Theo.	Actual		
Lauric	78	140	119	11	100
Lauric Hexane Purified	80	147	133	3.2	46
Stearic	105	97	99	8.7	96
Stearic Hexane Extract 1st	106	112	115	19	37
Stearic Hexane Extract 2nd	107	112	109	5.2	25

Blends of various proportions of the phenothiazine amides were made with various mineral oil lubricants. Table II reports the results of tests made upon some of these blends containing a lubricating oil having a viscosity of 150 SUS at 100° F. The tests were conducted by placing a 100 ml. portion of a blend in a beaker which contained a weighed amount of copper and lead particles. Air was bubbled into the liquid at a rate of 5 liters per hour. Pentane insolubles were determined by centrifuging the fluid upon completion of the test. A blank was run on a portion of lubricating oil which contained no phenothiazine amide inhibitor.

Table II

FIVE HOURS OXYGEN ABSORPTION TEST 360° F. (CuPb)

Phenothiazine Amide of—	Amide Sample No.	Percent Conc. in Oil	cc. O_2 Absorbed	Percent Vis. Rise	Catalyst Wt. Chge. (Milligrams)	C_5 Insol.	Acid No.
Lauric Acid	78	0.5	240	6.3	−5.6	0.35	0.65
Lauric Acid Hexane Extract	80	1.0	390	6.7	−4.5	0.83	1.52
Stearic Acid Hexane Extract	106	1.0	495	6.8	−33	0.45	1.35
Blank			2,200 in 2.5 hrs.	19.0	+11.8	0.52	3.7

In another high temperature oxidation test, a 1% solution of crude lauric acid amide of phenothiazine in a solvent treated Mid-Continent neutral oil having a viscosity of about 600 SUS at 100° F. and 90 viscosity index, proved far superior to the neat oil. In this test 20 cc. of the oil was dripped over a 6" x 3" inclined piece of tared aluminum foil, over 5 hours, at 425° F. The foil increased in weight 38 milligrams when using the inhibited oil and over 100 mg. when using the neat oil.

These oxidation inhibitors were found to be effective in preserving the oxidation stability of greases exposed

to high temperatures. For example, greases were prepared having the following:

Composition	Parts By Weight	
Sample No.	A	B
Li soap of 12-OH stearic acid	15.00	15.00
di-isooctyl azelate	83.78	84.78
Water	0.07	0.07
Free oleic acid	0.15	0.15
Phenothiazine stearyl amide	1.00	
NORMA-HOFFMAN BOMB OXIDATION		
P.s.i. Drop:		
100 hours	2	
130 hours		55
500 hours	5	

I claim:

1. A lubricant composition consisting essentially of a lubricant base selected from the group consisting of mineral oil lubricants and synthetic ester oil based metal soap thickened greases, and an oil-compatible fatty acid amide of phenothiazine, wherein the fatty acid radical contains 10 to 32 carbon atoms, in an amount sufficient to give improved oxidation stability in the temperature range of about 300 to 450° F.

2. The composition of claim 1 in which the lubricant base is a mineral oil lubricant.

3. The composition of claim 2 in which the mineral oil lubricant is a mineral oil of lubricating grade.

4. The composition of claim 1 in which the lubricant base is a synthetic ester oil-metal soap thickened grease.

5. The composition of claim 4 wherein the amide is present in a range of about 0.1 to 2.0% of the total lubricant composition.

6. The composition of claim 5 in which the metal soap is lithium 12-hydroxy stearate.

7. The composition of claim 3 wherein the amide is present in a range of about 0.1 to 2% of the total lubricant composition.

8. The composition of claim 3 where the fatty acid radical is that of lauric acid.

9. The composition of claim 3 where the fatty acid radical is that of stearic acid.

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