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LUBRICATING COMPOSITIONS

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This invention relates to lubricants particularly suitable for lubrication under extreme operating conditions, such as under extreme pressure, high speed and high temperature conditions.

It is well known that the high pressure occurring in certain types of gears and bearings may cause a film of lubricant to rupture with consequent damage to the machinery. It has been shown that base lubricants such as mineral oil and/or synthetic oil can be improved with regard to their protective effect particularly on rubbing surfaces by the addition of certain substances, so that excessive wear, scuffing and seizure, which normally follow a break in the film of lubricant, can be prevented even under very unfavorable pressure and speed conditions. Lubricants possessing this highly desirable property are called extreme pressure lubricants.

It is known that certain elements or compounds containing elements of the type of chlorine, sulfur, phosphorus and lead are capable of imparting extreme pressure properties to base lubricants. Among the compounds heretofore used are notable lead soaps, phosphoric acid esters, free sulfur and organic sulfur-containing compounds and certain chlorinated organic compounds.

A principal objection to extreme pressure compounds of the above is that they are highly reactive with contacting surfaces causing etching, corrosion and discoloration of contacting surfaces. Another objection to reactive extreme pressure agents is that they alter the original chemical nature of the contacting surface and this, under certain conditions, is undesirable. Additionally, because of the activity of agents of the type under discussion they usually deplete rapidly resulting in, at the very best, only a temporary solution to extreme pressure lubrication.

It has now been discovered that improved extreme pressure lubricants can be obtained by incorporating into a base lubricant, minor amounts of three particular types of additives, the combination of which produces a synergistic effect resulting in a lubricating composition suitable for extreme pressure lubrication and particularly for gear lubrication. The three types of additives are: (*a*) boric acid; (*b*) a phosphatidic material of animal and/or vegetable origin and (*c*) oil-soluble heterocyclic five member ring compounds containing carbon, nitrogen and a chalcogen such as oxygen or sulfur (azole) such as oil-soluble alkyl substituted oxazoline and/or thiazolines and salts thereof.

Each of the above-mentioned compounds and class of compounds must be present in compositions of this invention at all times and each being present in amounts varying from about 0.001% to about 10% and preferably from about 0.1% to about 2% by weight.

The phosphatidic material which can be of vegetable or animal origin is a complex glyceride phosphoric acid ester such as lecithin or cephalin or mixtures and derivatives thereof. Phosphatides may be extracted from such oils as soya bean oils or from animal tissues by any

suitable means and may be used in their crude or purified form. If desired, these phosphatides may be heat treated, sulfurized, phosphorized and/or halogenated in order to oil-solubilize and enchance their lubricating properties.

The oil-soluble heterocyclic five member ring compounds as mentioned above can be exemplified by oil-soluble oxazoline, isoxazoline, isoxazole and the thia and selena derivatives and the like. The oxazolines may be derived from amino hydroxy compounds through their fatty amides, or the oxazolines may be made by reacting an amino hydroxy compound with a nitrile. Any other procedure may be followed to prepare these heterocyclic compounds.

In preparing the oxazolines through their fatty acid amides, a suitable amino hydroxy compound is reacted with a desirable aliphatic carboxylic acid at an elevated temperature to yield an amide. The temperature is then increased so as to split out water and form the oxazoline. The temperature for the initial amide formation and final oxazoline formation depends upon the reacting materials employed and generally is within the range of 150° to 170° C. for the initial reaction and around about 250° C. for the final rejection.

Examples of suitable hydroxy amino compounds are the primary aliphatic amine having the hydroxy group on the carbon atom adjacent to the carbon atom bearing the amino radical and specifically the following compounds may be mentioned although they are not to be construed as a limitation: monoethanolamine, diethanolamine, 2-methyl-2-amino-1 propanol; 2-amino-2-methyl-pentanediol-1; 2-ethyl-2-aminopropanediol-1,3; 2-amino-2-propyl-butanediol-1,4; 3-tris(hydroxy methyl) aminomethane; 2-amino-1-butanol; 2-amino-1-pentanol; 2-amino-1-ethanol; 2-amino-3-butanol; 3-amino-4-pentanol; 3-amino-4-hexanol; 2-amino-3-heptanol; 1-amino-1-ethylpropylisopropanol and the like.

The acids which may be used to prepare oxazolines from the above amino compounds are saturated and unsaturated organic acids such as acetic, propionic, butyric, caprioc, heptoic, caprylic, pelargonic, captic, undecylic, lauric, tridecylic, myristic, pentadecylic, palmitic, stearic, nondecylic, archidic acids; acrylic, butenic, critonic, pentenic, tiglic, hexenic, teracrylic, oleic, erucic acids; naphthenic acids and the like; as well as fatty acids derived from animal, vegetable and fish oils or from oxidation of petroleum.

If the oxazolines are prepared from amino hydroxy compounds as referred to above and nitriles, the nitriles which can be used are alkyl, aryl, alkoxyalkane, nitrile, e, g., (ethoxy methoxy) ethane nitrile, (ethoxy ethoxy) octane nitrile, (methoxy methoxy) ethane nitrile, and nitriles of hexane, octane, decane, dodecane, tetradecane, hexadecane, octadecene, and the like. Also if oxazolidines are used they may be prepared by reaction of a suitable amino hydroxy compound ethane nitrile, (ethoxy ethoxy) octane nitrile, (methoxy methoxy) ethane nitrile, and nitriles of hexane, octane, decane, dodecane, tetradecane, hexadecane, octadecane, and the like. Also if oxazolidines are used they may be prepared by reaction of a suitable amino hydroxy compound and an aldehyde. Thus oxazolidines may be prepared by reacting one mole of an amino monohydric alcohol with one mole of an aldehyde such as formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, benzaldehyde, ethyl hexaldehyde, propionaldehyde and the like.

If desired, the above nitrogen-containing compounds can be used in their salt form by reacting them with a suitable acid such as fatty acids and hydroxy fatty acids of at least 10 carbon atoms, polycarboxylic acids, aromatic substituted aliphatic acids, naphthenic acids, sulfonic acids, phosphoric acids and the like. Such acids

are: capric, lauric, myristic, palmitic, stearic, linoleic, oleic, hydroxy stearic, ricinoleic, phenylacetic, phenyl stearic, alkyl succinic, alkyl maleic, alkyl malic, alkyl tartaric, alkyl citric, petroleum sulfonic acids, the carboxylic acids obtained by oxidation of petroleum, tall oil acids, organic acid phosphates such as dilauryl acid phosphate and the like.

Examples of compounds of these nitrogen-containing compounds include 2-heptyl-4-hydroxy methyl-4-ethyl oxazoline, 2-octyl-4-hydroxymethyl-4-ethyl oxazoline, 2-octadecyl-4-hydroxy methyl-4-ethyl oxazoline, 2-hexadecyl-4,4-dimethyl oxazoline, 2-oleyl-2-oxazoline, 2-oleyl-4-methyl-4-hydroxymethyl-2-oxazoline, 2-undecyl-4-propyl-4-ethyl-5-methyl-2-oxazoline, 2-dodecyl-4-hydroxybutyl-2-oxazoline, 2-undecyl-4, 4-dimethyl-5-phenyl-2-oxazoline, 2-undecyl-4-methyl-4-lauroxymethyl-2-oxazoline, 2-heptadecadienyl-4-propyl-4-hydroxyethyl-2-oxazoline, dioctyloxazole ethyloctyloxazole, diethyloctyloxazole, diheptyloxazole, butyl-oxazolidine, diethyl-oxazolidine, diheptyl-oxazolidine, ethyloctyloxazolidine, propyloctyloxazoline, ethyloctylisoxazole, dioctylisoxazole, dibutylisoxazole, propylbutylisoxazole, 2-oleyl-2-thiazoline, 2-oleyl-4-methyl-4-hydroxymethyl-2-thiazoline, 2-oleyl-2-selenazoline and the like. Compounds of the above types are sold by Commercial Solvents Corporation under the trade name of "Alkaterge-C," "Alkaterge-O" and "Alkaterge-T."

Salts of the above nitrogen containing compounds can be prepared by treating them with suitable acids as mentioned above under conditions described in U. S. Patent 2,402,791. Examples of such salts include 2-oleyl-4-methyl-4-hydroxymethyl-2-oxazoline, 2-heptyl-4-hydroxymethyl-4-ethyl oxazoline, 2-undecyl-4-propyl-4-ethyl-5-methyl-2-oxazoline, 2-heptadecyldienyl-4-propyl-4-hydroxyethyl-2-oxazoline, 2-oleyl-2-oxazoline, 2-oleyl-2-thiazoline, "Alkaterge-C," "Alkaterge-O," "Alkaterge-T" laurate, stearate, oleate, ricinoleate, lactate, citrate, tartrate, petroleum sulfonate, dilauryl, phosphate and mixtures thereof.

The base for additives of this invention can be any natural or synthetic material having lubricating properties. Thus the base may be a hydrocarbon oil obtained from a paraffinic, naphthenic, Midcontinent or Coastal stock and/or mixtures thereof. The viscosity of these oils may vary over a wide range such as from 40 SUS at 100° F. to 1000 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or with synthetic lubricants such as polymerized olefins, copolymers of alkylene, glycols and alkylene oxides, organic esters, e. g., 2-ethyl hexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran, polyalkyl silicone polymers, e. g., dimethyl silicone polymer and the like. If desired, the synthetic lubricants may be used as the sole base lubricant or admixed with fixed oils and derivatives thereof.

Compositions of this invention can be prepared by dissolving the phosphatidic material and heterocyclic nitrogen base or its salt or mixture thereof in the base lubricant. Boric acid is dispersed in water and a solvent such as dioxane and this solution is combined with the base lubricant containing the other two additives and the entire mixture heated while stirring to remove water and solvent and thereafter cooled. For example, (*a*) "Alkaterge-C" and lecithin were dissolved in mineral oil and the mixture was heated while stirring to around 100–110° C. and thereafter filtered warm to remove impurities. (*b*) Another solution is prepared by taking around 1.2 grams of boric acid, 1.8 grams of distilled water and 20 grams of dioxane and moving the mixture with stirring until a clear solution has been obtained.

Solutions (*a*) and (*b*) are combined and heated to around 132–135° C. while vigorously stirring and thereafter the composition is cooled.

Preferred compositions of this invention are illustrated by the following examples:

Composition A:	Percent by weight
Boric acid	0.34
"Alkaterge-C"	1.0
Animal lecithin	1.0
Mineral oil	Balance
Composition B:	
Boric acid	0.34
"Alkaterge-C" oleate	1.0
Animal lecithin	1.0
Mineral oil	Balance
Composition C:	
Boric acid	0.35
"Alkaterge-C"	0.75
Lecithin	0.75
Mineral oil	Balance
Composition D:	
Boric acid	0.35
2-heptyl-4-hydroxy-4-ethyl oxazoline	1.0
Lecithin	1.0
Mineral oil	Balance
Composition E:	
Boric acid	0.35
2-heptyl-4-hydroxy-4-ethyl oxazoline	1.0
Cephalin	1.0
Mineral oil	Balance
Composition F:	
Boric acid	0.35
Alkyl substituted oxazoline sulfonate	1.0
Lecithin	1.0
Mineral oil	Balance
Composition G:	
Boric acid	0.34
Alkyl substituted thiazoline	1.0
Lecithin	1.0
Mineral oil	Balance
Composition H:	
Boric acid	0.34
"Alkaterge-C"	1.0
Animal lecithin	1.0
"Ucon 50 HB–280X" (polyethylene oxide synthetic lubricant manufactured by Carbide and Carbon Chemical Corp.)	Balance

Compositions of this invention were evaluated for their extreme pressure properties on a spur-gear machine, which essentially consists of two geometrically similar pairs of gears connected by two parallel shafts. The gear pairs are placed in separate boxes, which also contain the supporting ball bearings. One of the shafts consists of two sections connected by a coupling. Loading is accomplished by locking one side of the coupling and applying torque to the other. The conditions of the spur-gear test were: 3000 R. P. M. pinion speed; ambient temperature; 10 cc./sec. flow rate. At full tooth face contact, mineral oil carried a tooth load (lb./inch face) of 432, while Compositions A and B of this invention each carried loads of over 5760. On the other hand compositions comprising (1) mineral oil containing 0.75% lecithin and 0.75% "Alkaterge-C" carried a load of only 2160; while Compositions (2) mineral oil containing 0.34% boric acid and 2% lecithin; (3) mineral oil containing 0.34% boric acid and 2% "Alkaterge-C"; (4) mineral oil containing 0.34% boric acid and 2% Na petroleum sulfonate and (5) mineral oil containing 0.34% boric acid and 2% Ca petroleum sulfonate were unstable and could not be tested reliably.

The above compositions were tested for stability by storing them in sample bottles at room temperature and observing the time it took for the boric acid to separate out of the oil. Compositions A and B did not show signs of separation in over 30 days, while Compositions 2, 3, 4 and 5 showed phase separation in less than one day.

Compositions of this invention can be combined with

other additives in lubricants, such as blooming agents, pour point depressants or viscosity improvers, anti-foaming agents, e. g., dimethyl silicone polymer and the like.

Antioxidants comprise several types, for example, alkyl phenols such as 2,4,6-trimethyl phenol, pentamethyl phenol, 2,4-dimethyl-6-tertiarybutyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-ditertiary-butyl-4-methyl phenol, 2,4,6-tri-tertiary-butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl amine, N-phenyl-beta-naphthylamine, N-phenyl-alpha-naphthylamine, dinaphthyl amine.

Corrision inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms; organic compounds containing acidic radicals in close proximity to a nitrile, nitro or nitroso group (e. g., alpha cyano stearic acid).

Wear reducing agents which may be used comprise: esters of phosphorus acids such as triaryl, alkyl hydroxy aryl, or aralkyl phosphates, thiophosphates or phosphites and the like; neutral aromatic sulfur compounds of relatively high boiling temperatures such as diaryl sulfides, diaryl disulfides, alkyl aryl disulfides, e. g., diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and trisulfides, and the like; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g., sperm oil, jonoba oil, etc.; in which the sulfur is strongly bonded; sulfurized long chain olefins such as may be obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils or acids, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with sulfurized hydroxy fatty acids; chlorinated hydrocarbons, such as chlorinated paraffin aromatic hydrocarbons, terpenes, mineral lubricating oil, etc.; or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g., urethanes, allophanates, carbazides, carbazones, etc.; polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds.

Depending upon the primary additives used and conditions under which they are used, the amount of secondary additives used may vary from 0.01 to 2% or higher.

This application is a continuation-in-part of our copending patent application Serial No. 299,742, filed July 18, 1952, now abandoned.

We claim as our invention:

1. A clear lubricating oil composition stable against phase separation comprising a major amount of a mineral lubricating oil and from about 0.1% to about 2% by weight each of boric acid, lecithin and an oil-soluble 2-alkyl oxazoline compound containing in the 4-position a polar radical selected from the group consisting of a hydroxyl radical and a hydroxyalkyl radical.

2. A clear lubricating oil composition stable against phase separation comprising a major amount of a mineral lubricating oil and from about 0.1% to about 2% by weight each of boric acid, lecithin and an oil-soluble salt of an 2-alkyl oxazoline compound containing in the 4-position a polar radical selected from the group consisting of a hydroxyl radical and a hydroxyalkyl radical.

3. A clear lubricating oil composition stable against phase separation comprising a major amount of a mineral lubricating oil and from about 0.1% to about 2% by weight each of boric acid, lecithin and an oil-soluble 2-alkyl-4 hydroxy-4-alkyl oxazoline oleate.

4. A clear lubricating oil composition stable against phase separation comprising a major amount of a mineral lubricating oil and from about 0.1% to about 2% by weight each of boric acid, lecithin, and an oil-soluble 2-alkyl-4 hydroxy-4-alkyl oxazoline petroleum sulfonate.

5. A clear lubricating oil composition stable against phase separation comprising a major amount of mineral lubricating oil, about 0.34% boric acid, and about 1% each of lecithin and an oil-soluble 2-alkyl oxazoline compound containing in the 4-position a polar radical selected from the group consisting of a hydroxyl radical and a hydroxyalkyl radical.

6. A clear lubricating oil composition stable against phase separation comprising a major amount of mineral lubricating oil, about 0.34% boric acid, and about 1% each of lecithin and an oil-soluble 2-alkyl-4 hydroxy-4-alkyl oxazoline oleate.

7. A clear lubricating oil composition stable against phase separation comprising a major amount of mineral lubricating oil, about 0.34% boric acid, and about 1% each of lecithin and an oil-soluble 2-alkyl-4 hydroxy-4-alkyl oxazoline petroleum sulfonate.

8. A clear lubricating oil composition stable against phase separation comprising a major amount of mineral lubricating oil, about 0.34% boric acid, and about 1% each of lecithin and an oil-soluble 2-heptyl-4-hydroxy-4-ethyl oxazoline.

9. A clear lubricating oil composition stable against phase separation comprising a major amount of mineral lubricating oil, about 0.34% boric acid, and about 1% each of lecithin and an oil-soluble 2-heptyl-4-hydroxy-4-ethyl oxazoline oleate.

10. A clear lubricating oil composition stable against phase separation comprising a major amount of mineral lubricating oil, about 0.34% boric acid, and about 1% each of lecithin and an oil-soluble 2-heptyl-4-hydroxy-4-ethyl oxazoline petroleum sulfonate.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 23,184	Whitbeck	Dec. 20, 1949
2,053,474	Graves	Sept. 8, 1936
2,530,837	Orozco	Nov. 21, 1950
2,564,423	Barnum	Aug. 14, 1951
2,587,955	Barnum	Mar. 4, 1952
2,614,985	Cook	Oct. 21, 1952