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UTILIZATION OF PHOSPHORIC ACID IN THE PREPARATION OF GREASES

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This invention relates to lubricating grease compositions, and more particularly to high temperature lubricating greases thickened with neutralized products of a blend of low molecular weight carboxylic acids, high molecular weight carboxylic acids and phosphoric acid. The lubricating grease compositions of the invention have outstanding extreme pressure characteristics in addition to other desirable grease characteristics.

In brief, this invention relates to the utilization of phosphoric acid directly in combination with a low molecular weight carboxylic acid having from about 1 to 3 carbon atoms per molecule and a high molecular weight carboxylic acid having from about 12 to 30 carbon atoms per molecule. These blends of phosphoric acid and organic carboxylic acids are neutralized with metal hydroxides or carbonates to provide the grease thickening agents of this invention.

The use of small amounts of a metal salt of phosphoric acid in lubricating grease compositions has been suggested in the prior art. In U.S. Patent No. 2,513,680 to Schott and Armstrong, for example, less than about 2.0% by weight of calcium phosphate is employed to improve the "skin hardening" and storage stability properties of calcium base greases thickened with a large amount of calcium soap. The use of more than about 2.0% by weight of phosphoric acid is taught to be definitely detrimental, and higher amounts to be positively destructive.

It has now been found that excellent lubricating grease compositions can be prepared by utilizing from about 2.5 to 10 wt. percent, preferably from about 2.5 to 6 wt. percent, of phosphoric acid in combination with about 10 to 15 wt. percent of a low molecular weight carboxylic acid such as acetic acid and about 2 to 10 wt. percent of a high molecular weight carboxylic acid such as stearic acid. As previously stated, the lubricating grease compositions of the invention are particularly characterized by high dropping points and outstanding load carrying properties. The greases exhibit these properties regardless of whether they are prepared in either the hydrous or anhydrous form.

It is not known exactly what reactions the phosphoric acid enters into during the preparation of the greases of this invention. However, for the present purposes it is sufficient to note that stable lubricating grease compositions are prepared by the use of blends of the low molecular weight carboxylic acids, phosphoric acid and high molecular weight carboxylic acids, wherein the phosphoric acid contributes in some manner to the production of effective lubricating grease compositions. The phosphoric acid may be utilized in concentrations ranging from about 5 to 100%.

Suitable low molecular weight carboxylic acids are the saturated and unsaturated aliphatic carboxylic acids having from about 1 to 3 carbon atoms per molecule. Examples of such acids include formic acid, acetic acid, propionic acid, etc. Acetic acid is preferred and may be either glacial acetic acid or an aqueous solution thereof, the concentration of the acetic acid in the aqueous solution varying from about 60 to 99.9 wt. percent. Substituted acetic acids having two carbon atoms per molecule such as chloro-acetic acid, glycolic acid, thioglycolic acid, glycine, etc. may also be used to modify the structure of lubricating grease compositions made in accordance with this invention. The amount of low molecular weight carboxylic acid employed will be within the range of about 10 to 15 wt. percent, preferably about 10 to 12 wt. percent, based on the total lubricating grease composition.

High molecular weight carboxylic acids containing from about 12 to 30, preferably about 18 to 22, carbon atoms per molecule are useful for the purposes of the present invention. These acids may be derived from saturated or unsaturated naturally occurring or synthetic fatty material. The fatty acids normally used in the manufacture of conventional greases, particularly the more saturated acids, are preferred. Examples of such acids include lauric, myristic, palmitic, stearic, mono- and poly-hydroxy stearic and arachidic acids as well as hydrogenated fish oil and tallow acids. Unsaturated fatty acids such as oleic, ricinoleic and similar acids may also be used. The amount of high molecular weight fatty acids employed in preparing the lubricating compositions of this invention will be from about 2 to 10 wt. percent, preferably about 2 to 5 wt. percent, based on the total lubricating grease composition.

In general, the mol ratio of low to high molecular weight carboxylic acids will range from about 10:1 to 30:1, preferably about 15:1 to 25:1, and the mol ratio of the average of the low molecular weight acids, i.e. the low molecular weight carboxylic acids and the phosphoric acid, to the high molecular weight carboxylic acids will be from 20:1 to 35:1, preferably about 25:1 to 30:1.

The metals suitable for neutralizing the above blend of acids are the alkaline earth metals: calcium, barium, magnesium and strontium. The above metals are generally employed in the form of hydroxides or carbonates, and the process of this invention will utilize from about 8 to 15 wt. percent, based on the total lubricating grease composition, of the metal hydroxide or carbonate. Calcium hydroxide is preferred. Mixtures of the above metals may also be employed, if desired.

The lubricating oils employed as the menstrua of the lubricant compositions of this invention may be either conventional grease-making mineral oils or synthetic lubricating oils. In general, the mineral and synthetic lubricating oils should have a viscosity within the range of about 50 to 2000 S.U.S. at 100° F. and about 30 to 220 S.U.S. at 210° F., an ASTM pour point of about +20 to −75° F., a flash point of about 350° to 650° F., and a viscosity index of about 0 to 60, although lubricating oils having a viscosity index of 100 or higher can also be employed.

The synthetic lubricating oils include esters of monobasic acids (e.g. an ester of C_8 Oxo alcohol with C_8 Oxo acid, an ester of C_{13} Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e.g. di-2-ethyl hexyl sebacate, di-nonyl adipate, etc.), esters of glycols (e.g. C_{13} Oxo acid diester of tetraethylene glycol, etc.), complex esters (e.g. the complex ester formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl-hexanol, a complex ester formed by reacting one mole of azelaic acid, one mole of tetraethylene glycol, one mole of C_8 Oxo alcohol and one mole of C_8 Oxo acid, etc.), esters of phosphoric acid (e.g. the ester formed by contacting three moles of the mono-methyl ether of ethylene glycol with one mole of phosphorous oxychloride, etc.), halocarbon oils (e.g. the polymer of chlorotrifluoroethylene containing twelve recurring units of chlorotrifluoroethylene), alkyl silicates (e.g. methyl polysiloxanes, ethyl polysiloxanes, methyl-phenyl polysiloxanes, etc.), sulfite esters (e.g. the ester formed by reacting one mole of sulfur oxychloride with two moles of the methyl ether of ethylene glycol, etc.), carbonates (e.g. the carbonate formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptals (e.g. the mercaptal formed by reacting 2-ethyl hexyl mercaptan with formaldehyde), formals (e.g. the formal formed by reacting C_{13} Oxo alcohol with formaldehyde), polyglycol type synthetic oils (e.g. the compounds formed by condensing butyl alcohol with fourteen units of propylene oxide, etc.), or mixtures of the above in any proportions.

The lubricating grease compositions of the invention will contain from about 50 to 90 wt. percent, preferably about 65 to 85 wt. percent, of the mineral and/or synthetic lubricating oil and about 10 to 50 wt. percent, preferably about 15 to 35 wt. percent, of the reaction products of blends or mixtures of the above acids with the metal base.

Conventional lubricating grease additives may also be employed in the lubricating grease compositions of the present invention. Such additives, for example, include: oxidation inhibitors such as phenyl alpha naphthylamine, corrosion inhibitors such as sorbitan monooleate, tackiness agents such as polyisobutene or high molecular weight polymerized acrylic esters, and the like.

In general, the lubricating grease compositions of this invention may be prepared by coneutralizing the blend or mixture of phosphoric acid, the low molecular weight carboxylic acids and the high molecular weight carboxylic acids with the metal base, e.g. hydrated lime, and dispersing the products in the lubricating oil. It is not essential that the water of reaction be removed. However, a somewhat greater stability can be achieved when the water of reaction is removed by carrying out the grease preparation at elevated temperatures.

The preferred method of preparing the lubricating grease compositions of this invention involves mixing the metal base and the lubricating oil together at room temperature to form an intimate slurry. The high molecular weight carboxylic acid is added to the slurry with stirring. A blend of the low molecular weight carboxylic acid and the phosphoric acid is then added with continued mixing, and a solid grease forms almost instantaneously with the temperature rising to about 180° to 210° F. Conventional lubricating grease additives such as phenyl alpha naphthylamine can be added at this temperature, and the stirring is continued until the temperature has subsided to about 100° to 140° F. The resulting grease composition may then be finished by passage through a Morehouse mill or Gaulin homogenizer at pressures of about 3,000 to 8,000 p.s.i. and at high rates of shear within the range of about 100,000 to 500,000 reciprocal seconds.

If desired, the lubricating grease compositions of this invention may also be prepared by heating the grease batch to a temperature of about 400° to 550° following the addition of the blend of low molecular weight carboxylic acid and phosphoric acid. The heated grease batch is then cooled to a temperature of about 150° to 180° F. with stirring and the conventional grease additives charged. This lubricating grease composition may also be finished by homogenization.

The invention will be more fully understood by reference to the following specific examples illustrating various modifications of the invention.

EXAMPLE I

A lubricating grease composition according to this invention was prepared from the following constituents:

Formulation	Percent Weight
Glacial acetic acid	12.0
Stearic acid	3.0
Phosphoric acid (85% conc.)	3.0
Hydrated lime	10.9
Phenyl alpha naphthylamine	0.5
Mineral lubricating oil, 55 SUS @ 210° F.	70.6
Mol ratio of acetic acid to stearic acid	20:1
Mol ratio of low mol. wt. acids (i.e. acetic acid plus phosphoric acid) to stearic acid	22.8:1

Preparation

The hydrated lime and the mineral lubricating oil were mixed together at room temperature (about 70° F.) to form an intimate slurry. The stearic acid as a powder was added to the lime slurry. A blend of the acetic and phosphoric acid was then added. A solid grease formed immediately with the temperature rising to about 190° F. The phenyl alpha naphthylamine was added, and the stirring continued for about two hours until the temperature subsided. The grease was homogenized by being passed through a Morehouse mill.

Properties

Appearance	Excellent, uniform product.
Dropping point, ° F.	500+.
Penetration, 77° F. mm./10:	
Unworked	220.
Worked 60 strokes	250.
Worked 75,000 strokes	298 (108° F.).
Phase change up to 450° F.	None.
E.P. properties, Timken test (50 lbs. load)	Pass, narrow scar.
Lubricating life, hrs. (10,000 r.p.m. @250° F.)	804.

The above data show that the lubricating grease compositions encompassed by this invention have very desirable high temperature stability and extreme pressure characteristics.

EXAMPLE II

Formulation	Percent Weight
Glacial acetic acid	12.0
Stearic acid	3.0
Phosphoric acid (85% conc.)	3.0
Hydrated lime	11.6
Phenyl alpha naphthylamine	0.5
Mineral lubricating oil, 55 SUS @ 210° F.	69.9
Mol ratio of acetic acid to stearic acid	20:1
Mol ratio of low mol. wt. acids (i.e. acetic acid plus phosphoric acid) to stearic acid	22.8:1

Preparation

Similar to that described in Example I, except that following the addition of the blend of acetic acid and phosphoric acid the grease mixture was heated to a temperature of about 500° F. The resulting grease composition was then cooled to about 200° F. with stirring, and the phenyl alpha naphthylamine added. The grease was then Gaulin homogenized at 6500 p.s.i.

Properties

Appearance	Excellent, uniform product.
Dropping point, °F.	500+.
Penetration, 77° F. mm./10:	
Unworked	210.
Worked 60 strokes	230.
Worked 230,000 strokes	300 (118° F.).
Cooled to 77° F. reworked 60 strokes	330.
Phase change up to 450° F.	None.
E. P. properties, Timken test (50 lbs. load)	Pass, narrow scar.
Norma Hoffman oxidation test (hrs. to 5 p.s.i. drop)	420.
Lubrication life, hrs. (250° F.—10,000 r.p.m.)	[1]1200+.

[1] No failure—test discontinued.

The grease of Example II also showed the desired high temperature, stability and load carrying properties of the grease prepared in accordance with the method described in Example I, though the former was prepared at a much higher temperature to effect dehydration.

It will be further understood that the present invention is not necessarily limited to the specific materials and conditions of the foregoing examples. These materials and conditions may be varied within the limits indicated in the general portions of the specification.

What is claimed is:

1. A lubricating grease composition comprising a major proportion of lubricating oil thickened with a grease thickening amount of an alkaline earth metal base neutralized mixture of high molecular weight monocarboxylic acids having about 12–30 carbon atoms per molecule, low molecular weight monocarboxylic acids having from about 1–3 carbon atoms per molecule, and phosphoric acid, the amount of said phosphoric acid being 2.5 to 10.0 wt. percent, wherein the mole ratio of low molecular weight acids to high molecular weight carboxylic acid is about 20:1 to 35:1 and wherein the mole ratio of said low molecular weight carboxylic acid to said high molecular weight carboxylic acid is about 10:1 to 30:1.

2. The composition of claim 1 wherein said alkaline earth metal base is a calcium base.

3. The composition of claim 1 wherein said lubricating oil is a mineral lubricating oil.

4. A lubricating grease composition comprising a major amount of mineral lubricating oil and about 10 to 50 wt. percent of the alkaline earth metal salts of a C_{12} to C_{30} fatty acid, a C_1 to C_3 fatty acid and phosphoric acid, the amount of phosphoric acid being about 2.5 to 10.0 wt. percent, wherein the mole ratio of low molecular weight acids to high molecular weight carboxylic acid is about 20:1 to 35:1, and wherein the mole ratio of acetic acid to said C_{12} to C_{30} fatty acid is about 10:1 to 30:1.

5. A grease composition according to claim 4, wherein said alkaline earth metal is calcium and said C_1 to C_3 fatty acid is acetic acid.

6. The method of preparing a lubricating grease composition which comprises dispersing a metal base in a lubricating oil, adding to the resulting dispersion high molecular weight carboxylic acids having from about 12 to 30 carbon atoms per molecule, then adding a blend of low molecular weight carboxylic acids having about 1 to 3 carbon atoms per molecule and phosphoric acid wherein the mole ratio of low molecular weight carboxylic acid to high molecular weight carboxylic acid is about 10:1 to 30:1 and wherein the mole ratio of said low molecular weight carboxylic acid and said phosphoric acid to said high molecular weight carboxylic acid is about 20:1 to 35:1 and thereafter cooling the resulting grease mixture to obtain said lubricating grease composition, said metal base being present in sufficient amounts to neutralize said acids and the amount of said phosphoric acid being 2.5 to 10.0 wt. percent.

7. The method of claim 6 wherein said grease mixture is heated to a temperature of about 400° to 550° F. subsequent to the addition of the blend of low molecular weight carboxylic acid and phosphoric acid.

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