LUBRICANTS CONTAINING MIXED METAL SALTS OF FATTY ACID AND AROMATIC POLYBASIC ACID

Arnold J. Morway, Clark, N.J., assignor to Eso Research and Engineering Company, a corporation of Delaware

No Drawing

Filed Apr. 1, 1964, Ser. No. 356,661

6 Claims. (Cl. 252—41)

This invention relates to lubricants comprising lubricating oil containing alkali metal mixed salts of fatty acids and certain aromatic polybasic acids as additives or as grease thickeners.

In its preferred form, the invention relates to lubricating grease suitable for lubrication of anti-friction bearings comprising lubricating oil thickened with a mixture of alkali metal salt of fatty acid, which is preferably a mixture of low molecular weight fatty acid and a higher molecular weight fatty acid, and aromatic polycarboxylic acid, in certain molar equivalent proportions. The greases of the invention differ from previously known, related alkali metal high temperature bearing greases wherein the thickener is a mixed salt of low molecular weight fatty acid, e.g., acetic acid, and higher molecular weight fatty acid, e.g., C14 to C30 fatty acid. Thus, in contrast to said previously known greases, the greases of the invention do not become excessively fluid at elevated temperatures, or become excessively rubbery or fibrous at elevated temperatures, due to phase changes in the soap-thickening structure.

The mixed-salt systems of the invention are best made to contain alkali metal salt of 0.5 to 6.0, preferably 2 to 4, molar hydrogen equivalents of low molecular weight C2 to C5 fatty acid per molar hydrogen equivalent of aromatic polycarboxylic acid. These systems will also contain salt of 0.5 to 3.0, preferably 1 to 2 molar hydrogen equivalents of higher molecular weight fatty acid, e.g., C14 to C30 fatty acid, per molar hydrogen equivalent of said aromatic acid. Greases can be thus prepared having a total content of these carboxylic acid salts of 5.0 to 40.0 weight percent, preferably 10 to 35 weight percent, based on the weight of the grease. These greases in turn can be diluted with additional oil to form fluid or semifluid compositions containing about 0.1 to 5.0% of the mixed salt.

Suitable low molecular weight fatty acids include C2 to C5 fatty acid such as acetic, propionic, butyric, etc. Acetic acid or its anhydride is preferred.

The high molecular weight fatty acid includes C16 to C30 naturally-occurring or synthetic, substituted or unsubstituted, saturated or unsaturated, mixed or unmixed fatty acids. Preferred acids will have 16 to 24 carbon atoms per molecule. Examples of such acids include myristic, palmitic, stearic, 12-hydroxy stearic, arachidic, oleic, ricinoleic, hydrogenated fish oil, tallow acids, etc.

The aromatic polycarboxylic acids used in this invention are those having 2 to 4 carboxylic acid groups per benzene ring, which carboxylic acid groups can be in the ortho, meta or para position. These aromatic acids in-
It has been further found that conneutralizing phosphoric acid along with the other acids can further improve the lubricant. Specifically, not only does a harder grease result but the metal phosphate imparts anti-oxidation properties and increases the lubrication life of the grease. Usually, about 0.1 to 6.0, preferably 1.0 to 5.0 wt. percent, of ortho phosphoric acid will be used.

The lubricants of the invention can be formed in a number of different ways. The most convenient is to neutralize the acids, in at least a portion of the oil, with an aqueous solution, e.g. 10 to 90 wt. percent water, of the alkali metal base. Usually, the grease will be milled to a smooth consistency before dehydrating since the wet grease is easily homogenized or milled. Usually, the resulting composition will then be heated and dehydrated at about 300° to 550° F., preferably 400 to 500° F., then cooled, and any additives used are then added. Usually, the cooled grease will be further homogenized.

Various other additives may also be added to the lubrication composition (e.g. 0.1 to 10.0 wt. percent) of oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors such as sodium nitrite and sorbitan monooleate; dyes; extreme pressure agents; tackiness agents; other grease thickeners, and the like.

The invention will be further understood by reference to the following examples wherein all parts are by weight.

**EXAMPLE I**

72.2 parts of mineral lubricating oil of about 60 SUS viscosity at 210° F., 15 parts of Hydrofol Acid 51 and 3 parts of phthalic anhydride were added to a fire-heated kettle and stirred while heating to 130° F. Then 5.8 parts of lithium hydroxide monohydrate, in the form of an aqueous solution consisting of 20 wt. percent of said monohydrate and 80 wt. percent water, was added to the mixture. This was followed immediately by the addition of 3 parts of glacial acetic acid. The neutralized composition was then mixed for 30 minutes, after which the wet grease, which had a temperature of about 200° F., due to the heat of reaction, was cycled through a Charlotte mill having an 0.008" opening and then passed back to the kettle until all lumps and small specks had been eliminated and a smooth homogeneous grease was obtained. Without milling at this stage, the small specks of undisperssed salts and soaps, if heated and dehydrated, cannot be effectively eliminated by milling at a latter stage. The smooth, wet milled grease was then heated to a temperature of about 440° F., which was maintained for about one-half hour in order to dehydrate and fully disperse the salts in the oil. Heating was then discontinued and the grease was allowed to cool to 250° F. where one part of phenyl-alpha-naphthylamine was added. The grease was then cooled to 120° F. and passed again through the Charlotte mill to form a finished grease.

The Hydrofol Acid 51 used above is hydrogenated fish oil having a degree of unsaturation and average chain length similar to stearic acid.

**EXAMPLE II**

78.36 parts of mineral lubricating oil (60 SUS viscosity at 210° F.), 10.85 parts of Hydrofol Acid 51 and 2.01 parts of phthalic anhydride were added to a fire-heated kettle and stirred while heating to 130° F. Then, 3.9 parts of lithium hydroxide monohydrate in the form of an aqueous solution (20 wt. percent lithium hydroxide monohydrate) was added, followed immediately by the addition of 2.01 parts of glacial acetic acid. After mixing for 30 minutes, the wet grease which was now at a temperature of about 200° F. was passed through a Charlotte mill having an 0.003" clearance and recycled back to the kettle until homogeneous grease was obtained. The smooth, wet, milled grease was then heated to a temperature of about 440° F., which was maintained for about 0.5 hour, in order to completely dehydrate and complex the salt composition. Heating was then discontinued and the grease was cooled to 250° F., where 0.67 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor. The grease was then further cooled to 120° F., after which 3 parts of a 50/50 by weight mixture of sodium nitrite dispersed in mineral lubricating oil having a viscosity of 300 SUS at 100° F. was added. The sodium nitrite used here had an average particle size of about 30 microns. After the sodium nitrite dispersion was added, the grease was then homogenized by passage through a Charlotte mill.

**EXAMPLE III**

A grease was prepared in the same manner as that of Example II except that pyromellitic dihydride was used in place of the phthalic anhydride and the proportions of the various ingredients differed from those of Example II.

**Composition A**

A grease was prepared representing the prior art and which was similar to the greases of the examples except that no aromatic acid was used. This grease was prepared as follows:

76.8 parts of mineral lubricating oil and 15 parts of Hydrofol Acid 51 were added to a fire-heated kettle and stirred while heating to 130° F. Then 4.3 parts of lithium hydroxide monohydrate in the form of an aqueous solution (20 wt. percent lithium hydroxide monohydrate) was added to the mixture, followed immediately by the addition of 3 parts of glacial acetic acid. The composition was then mixed for 30 minutes, after which the wet grease, which had a temperature of about 140° F., was cycled through a Charlotte mill having an 0.003" opening and then passed back to the kettle until all lumps and small specks had been eliminated. The smooth, wet milled grease was then heated to a temperature of about 440° F., which temperature was maintained for about one-half hour in order to dehydrate and complex the mixture. Heating was then discontinued and the grease allowed to cool to 250° F., where one part of phenyl-alpha-naphthylamine was added. The grease was then cooled to 120° F. and homogenized in a Gaulin homogenizer to form a finished grease.

**Composition B**

This grease was a simple lithium hydroxy stearate grease and represents a grease without salts of either the low molecular weight fatty acid or the aromatic acid. This grease was prepared as follows:

10 parts of 12-hydroxy stearic acid was charged to a fire-heated kettle along with 87.5 parts of mineral lubricating oil and mixed while heating to 130° F. Then 1.5 parts of lithium hydroxide monohydrate (in the form of an aqueous solution containing 20 wt. percent lithium hydroxide monohydrate) was added. Heating was then initiated and the composition was heated to a temperature of 390° F., which was maintained for about one-half hour and the entire composition was totally dehydrated. The composition was then cooled to 250° F., where one part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor. The composition was then cooled to 120° F. and then homogenized in a Morehouse mill, after which it was packaged.

The formulations of the above examples and com-
As seen by the preceding table, the compositions of the invention represented by Examples I and II have higher dropping points, greater stability against working, and a longer lubrication life at 250° F., when compared to the comparison Composition A which is formed from the same ingredients but without the phthalic anhydride. It is to be noted that the total amount of thickener of Composition A lies between that of Examples I and II so that these differences in properties are not due to a difference in the amount of total salt thickener present. Also, Examples I and II are seen to be superior to Composition B with regard to dropping point and lubrication life at 300° F. Composition B represents a commercially successful lithium grease which has found widespread use as a multi-purpose grease, but which is limited in its use at high temperatures.

In addition, the greases of Examples I and II were excellent ball bearing greases as demonstrated by a Ball Bearing Temperature Rise Test. In this test, a 204 mm. steel ball bearing is packed with 3.0 grams of grease, and then the bearing is operated at 10,000 r.p.m. while the temperature of the bearing was measured by thermocouples placed on the outer bearing race. After ten minutes in this test, using the grease of Example I, the bearing reached its maximum rise temperature of 10° F. above room temperature (75° F.) and then began to drop. This indicates that the grease was an excellent, quick-channeling grease. That is, the grease had quickly formed a channel for the rotating balls. Such channeling properties are important for ball bearing greases since it reduces power consumption which would otherwise be wasted by the churning of a non-channeling grease. The grease of Example II was also a quick-channeling grease, although a little slower than the grease of Example I. Specifically, the grease of Example II reached a maximum temperature rise of 20° F. above the room temperature (75° F.) in twenty minutes and then the temperature fell until it returned to about room temperature.

The grease of Example III was also an excellent grease, although it had a very faint grainy appearance. This grease also had a good high temperature lubrication life at 300° F., which was in excess of 500 hours and still running.

Asphaltic and soap base greases are generally well known in the field.

Amount of lubricating oil and about 5 to 40 wt. percent of alkali metal salt of C6 to C8 fatty acid, C10 to C30 fatty acid and a polycarboxylic acid consisting of a single benzene ring having 2 to 4 carboxy groups, in a mole equivalent ratio of about 0.5 to 6.0 mole equivalents of said C6 to C8 fatty acid per mole equivalent of said aromatic acid and about 0.5 to 3.0 mole equivalents of said C10 to C30 fatty acid per mole equivalent of said aromatic acid.

A lubricating grease according to claim 2 wherein said aromatic acid is phthalic acid.

A lubricating grease according to claim 3 wherein said alkali metal is lithium.

A lubricating grease consisting essentially of a major amount of mineral lubricating oil and about 10 to 35 wt. percent of aromatic acid, C10 to C30 fatty acid, and phthalic anhydride, in a relative mole equivalent ratio of about 2 to 4 mole equivalents of said aromatic acid per mole equivalent of said phthalic anhydride and about 1 to 2 mole equivalents of said C10 to C30 fatty acid per mole equivalent of said phthalic anhydride.

A lubricating grease consisting essentially of a major amount of mineral lubricating oil and about 10 to 35 wt. percent of aromatic acid, C10 to C30 fatty acid, and phthalic anhydride, in a relative mole equivalent ratio of about 2 to 4 mole equivalents of said aromatic acid per mole equivalent of said phthalic anhydride and about 1 to 2 mole equivalents of said C10 to C30 fatty acid per mole equivalent of said phthalic anhydride.