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# LUBRICATING GREASE THICKENED WITH LITHIUM SOAP OF STYRENATED FATTY ACID

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This invention relates to improved lubricating greases, and more particularly to lubricating greases thickened with lithium soaps of styrenated fatty acids.

I have found that styrenated fatty acid materials may be employed very successfully in the preparation of lithium base lubricating greases, either as the sole saponifiable material or in admixture with other saponifiable materials of conventional types. Lubricating greases are obtained in this manner having very superior shear resistance and other special properties as compared with lithium base greases prepared from conventional fatty acid materials, and in addition the use of such saponifiable materials permits the grease preparation to be carried out by the convenient low temperature method, wherein the saponification and dehydration are carried out at temperatures below the melting point of the soap.

The styrenated fatty acid materials which are employed as the saponifiable materials for producing the greases of this invention are addition products of unsaturated high molecular weight fatty acids and their esters with styrene. They are readily obtained by heating together the unsaturated fatty acid material and styrene, as described for example, by P. O. Powers, Industrial and Engineering Chemistry, volume 42, page 2097–99 (1950). The reaction apparently proceeds wtih saturation of the styrene double bond, producing unsaturated fatty acids having a phenyl ethyl group attached to one of the carbon atoms linked by the double bonds. Styrenated oleic acid is considered to be represented by the formula

$$\begin{array}{l} CH_3(CH_2)_7\underset{\substack{| \\ CH-CH_3 \\ | \\ C_6H_5}}{C}=CH(CH_2)_7COOH \end{array}$$

In addition to the sample monomeric addition products represented by this formula, the reaction product may contain various polymeric compounds containing more than one styrene particle for each fatty acid molecule and also compounds containing two or more carboxylic acid groups, obtained by cross-linking reactions.

Suitable starting materials for the styrenation reaction are unsaturated fatty acids containing at least 12 carbon atoms, such as from 12 to about 32 carbon atoms per molecule, and one or more olefinic double bonds per molecule, and the glycerides or other esters of such acids. They may be employed either in relatively pure form or in naturally occurring mixtures with each other and with minor proportions of saturated fatty acids and their esters derived from animal, vegetable or marine oils, such as, for example, lard oil, cottonseed oil, linseed oil, castor oil, menhaden oil, whale oil, etc. The preferred starting materials are those consisting of at least a predominant proportion of unsaturated fatty acids containing from about 16 to about 24 carbon atoms and either 1 or 2 olefinic double bonds per molecule, such as, for example, oleic acid, palmitolenic acid, lauroleic acid, palmitolic acids, petroselic acid, linoleic acid, eicosylenic acid, erucic acid and ricinoleic acid, and the esters of such acids.



The lubricating greases of this invention suitably contain from about 5 to about 50 percent by weight of the lithium soap of a styrenated fatty acid material as described above, either alone or in conjunction with other thickening agents such as different fatty acid soaps. With particular advantage, the thickening agent may comprise a lithium soap of styrenated fatty acid material together with a lithium soap of a different fatty acid material, such as unsubstituted fatty acids and hydroxy fatty acids of the types which have been employed heretofore in grease making, in a ratio of from about 1 to 3 to about 3 to 1 by weight, and preferably in a ratio of from about 1 to 2 to about 2 to 1 by weight.

The oleaginous liquids employed in these greases may be any oils suitable for use in grease making generally, such as mineral oils obtained by any of the conventional refining processes in the lubricating oil viscosity range, preferably those having viscosities from about 80 seconds Saybolt Universal at 100° F. to about 225 seconds at 210° F. For certain purposes, such as for producing greases suitable for high temperature operations, various synthetic oils may be employed with advantage, such as high molecular weight ethers, esters, and silicone polymer oils. Particularly suitable synthetic esters are dicarboxylic acid esters, such as, for example, di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, and di-2-ethylhexyl azelate.

The greases may also contain various additives of the usual types employed in lubricating greases, such as corrosion inhibitors, oxidation inhibitors, antiwear agents, etc. Preferably, they contain an oxidation inhibitor, which may suitably be an oxidation inhibitor of the amine type, such as diphenylamine, phenyl naphthylamine or tetramethyl diamino diphenyl methane.

The grease preparation may be carried out by any suitable grease making procedure. It is preferably carried out by the method involving saponification in situ, wherein the saponification of the styrenated fatty acid material, or a mixture of such material with other saponifiable fatty acid material as described above, is carried out in a portion of the lubricating oil employed as the liquid base. The oil employed in the saponification is preferably a mineral oil or other oil which is not hydrolyzed under the saponification conditions. Following the saponification, the saponification mass is heated at a higher temperature to dehydrate, and the main portion of the oleaginous liquid component and any additives employed are mixed in while the grease is allowed to cool.

The styrenated fatty acid material may be prepared by heating together the unsaturated fatty acid material and styrene at temperatures in about the range 150° to 300° C., employing the fatty acid material and styrene in a ratio from about 1 to 2 to 2 to 1 by weight. It is preferably carried out at temperatures in about a range 150–260° C. employing the fatty acid material and styrene in about equal amounts by weight.

The following examples are illustrative of the lubricating greases of this invention.

*Example I*

A grease was prepared having the following composition in percent by weight:

| | |
|---|---|
| Lithium soap of styrenated oleic acid | 16.5 |
| Phenyl alpha naphthylamine | 0.4 |
| Mineral lubricating oil | Remainder |

The mineral lubricating oil was a refined naphthene base distillate oil having a Saybolt Universal viscosity of 312 seconds at 100° F.

The styrenated oleic acid was prepared by heating together 1000 grams of oleic acid, having a neutralization number of 195, a saponification number of 197 and an iodine number of 84, and 1000 grams of styrene at 150° C. under reflux for 10 hours and then for an additional 16 hours at 150–260° C. The product was then cooled quickly by drawing in thin layers. A hard brittle solid was obtained having a neutralization number of 84, an iodine number of 41 and a melting point (Fisher Block) of 158–176° F.

The grease preparation was carried out in the following manner: A laboratory grease kettle was charged with 290 grams of the styrenated oleic acid, 300 grams of the mineral lubricating oil and 138 grams of 10 percent aqueous solution of lithium hydroxide. This mixture was heated for 1 hour at 200° F. until the saponification was complete and then at 300° F. for an additional hour to dehydrate. An additional 300 grams of the mineral lubricating oil was added while the temperature of the mass was maintained at 300° F., and 904 grams more of the oil was added gradually while the mixture was cooling from 300° F. to 220° F. The inhibitor was then added, and the grease finally drawn at 210° F. and finished by milling with two passes through a Premier Colloid Mill at 0.002 inch clearance.

The product obtained as described above was a tan slightly stringy grease which gave the following tests:

| | |
|---|---|
| Dropping point, ° F | 381 |
| Penetration, ASTM, at 77° F.: | |
| Worked 60 strokes | 271 |
| Worked 100,000 strokes | 313 |
| Dynamic water resistance test, percent loss | 4 |
| Norma-Hoffman oxidation test, 210° F., 100 hours, pressure drop, lbs | 2 |
| Grease breakdown machine test, 80–300° F.: | |
| Rating | Excellent |
| Leakage | None |

The Grease Breakdown Machine Test is a test for determining the ability of a grease to lubricate ball bearings at high rotative speeds and elevated temperatures. It is carried out as described in U.S. 2,600,058, column 6, lines 11–70, by rotating a ball bearing lubricated with the grease under test at 3450 r.p.m. at increasing temperatures up to 300° F. The grease rating depends upon the amount of change which the grease has undergone in the test.

*Example II*

A grease was prepared having the following composition in percent by weight:

| | |
|---|---|
| Lithium soap of styrenated oleic acid | 8.7 |
| Phenyl alpha naphthylamine | 0.2 |
| Mineral lubricating oil | 5.6 |
| Synthetic ester | Remainder |

The mineral lubricating oil was a refined paraffinic distillate oil having a viscosity of about 105 seconds Saybolt Universal at 100° F. The synthetic ester was a commercial di-2-ethylhexyl sebacate, having a Flash Point, COC, of 410° F., a kinematic viscosity of 100° F. of 1.83 centistokes, and a Pour Point below −65° F.

The styrenated oleic acid was the same as that described in Example I.

The grease preparation was carried out substantially as described in Example I, employing a kettle charge consisting of 580 grams of styrenated oleic acid, 400 grams of mineral oil and 515 grams of 10 percent aqueous solution of lithium hydroxide. The synthetic ester was added following the dehydration and during the cooling. The milling step was omitted.

The grease obtained had a dropping point of 400° F. and an ASTM worked penetration of 342. It gave a pressure drop of 3 pounds in the Norma-Hoffman oxidation test at 210° F.

*Example III*

A grease was prepared having the following composition in percent by weight:

| | |
|---|---|
| Lithium soap of styrenated oleic acid | 9.7 |
| Lithium stearate | 9.7 |
| Phenyl alpha naphthylamine | 0.5 |
| Mineral lubricating oil | Remainder |

The mineral lubricating oil was the same as that described in Example I.

The styrenated oleic acid was prepared by heating together 1,000 grams of oleic acid, having a neutralization and saponification number of 201 and an iodine number of 98, and 1,000 grams of styrene at about 150° C. under reflux for 5 hours, and then shock cooling the reaction product. A hard brittle solid was obtained having a neutralization number of about 20 and a saponification number of about 105.

The grease preparation was carried out employing a kettle charge consisting of 198 grams of the styrenated oleic acid, 196 grams of stearic acid, 260 grams of 10 percent aqueous lithium hydroxide solution, 400 grams of mineral oil and 400 grams of water. The saponification was carried out by heating the mixture for 2 hours at 210° F. and the dehydration was accomplished by heating for an additional hour at 310° F. After the dehydration, 400 grams more of the mineral oil were added while the temperature was maintained at 310° F., and an additional 850 grams were added during the cooling to 210° F. The inhibitor was then added and the grease was finally drawn at 204° F.

The uniform fibrous grease was obtained by the above procedure which gave the following tests.

| | |
|---|---|
| Dropping point ° F | 371 |
| Penetration, ASTM, 77° F.: | |
| Unworked | 247 |
| Worked 60 strokes | 275 |
| Worked 100,000 strokes | 328 |
| Norma-Hoffman oxidation 100 hrs. at 210° F., pressure drop, lbs | 1 |
| Dynamic water resistance test, loss, percent | 0 |
| Dynamic shear test: | |
| Miniature penetration— | |
| Original | 64 |
| After test | 42 |
| Water absorption test, water absorbed, percent | 35 |
| Miniature penetration: | |
| Original | 64 |
| After test | 112 |

The dynamic shear test is a test for measuring the resistance of a grease to texture change when worked under high shearing stress. The test apparatus comprises a perforated piston reciprocating within a closed cylinder maintained at a constant temperature. The test was carried out by charging a sample of the grease to the cylinder maintained at 225° F. and reciprocating the piston at 49 strokes per minute for 8 hours. Miniature penetrations were taken upon the grease both before and after the test. The miniature penetration test is described in Industrial and Engineering Chemistry, Analytical Edition, volume II, page 108 (February 15, 1939). As shown by the data, the grease of this invention gave only a small change in miniature penetration in this test, indicative of excellent shear stability. Greases thickened with lithium stearate break down in this test and become liquid or semi-liquid products.

As shown by the data, the greases of the above examples which are representative of the greases of this invention, had high dropping points of above 350° F., good oxidation resistance and resistance to water washing and absorption, and excellent working stability. In addition, they gave very good bearing lubrication in engine tests under actual service conditions.

Obviously many modifications and variations of the invention, as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A lubricating grease composition consisting essentially of a lubricating oil thickened to a grease consistency by a lithium fatty acid soap comprising at least 25 percent by weight of the lithium soap of a styrenated high molecular weight unsaturated fatty acid.

2. A composition according to claim 1 wherein the said styrenated unsaturated fatty acid is styrenated oleic acid.

3. A composition according to claim 1 wherein the said lubricating oil is a mineral lubricating oil.

4. A composition according to claim 1 wherein the said lubricating oil is a high molecular weight dicarboxylic acid di-ester.

5. A lubricating grease composition consisting essentially of a lubricating oil thickened to a grease consistency by a mixture in about 1:3 to 3:1 ratio by weight of lithium soap of a styrenated high molecular weight unsaturated fatty acid and lithium soap of an unsubstituted high molecular weight fatty acid.

6. A lubricating grease consisting essentially of a mineral lubricating oil thickened to a grease consistency by about 5 to 50 percent by weight of a mixture in about a 1:2 to 2:1 ratio by weight of lithium soap of styrenated oleic acid and lithium stearate.

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