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TWO-STAGE PREPARATION OF HIGH DROPPING POINT LITHIUM SOAP GREASE

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ABSTRACT OF THE DISCLOSURE

A high temperature multipurpose grease is prepared from the lithium soap of a C_{12} to C_{24} hydroxy fatty acid, e.g. 12-hydroxy stearic acid, and a dilithium soap of a C_4 to C_{12} dicarboxylic acid, e.g. dilithium azelate. A rigorous control of processing conditions, including two stages of heating, results in a good yield of grease of high dropping point.

BACKGROUND OF THE INVENTION

This invention is concerned with the preparation of a lithium soap grease having a high dropping point. Lithium soap greases have been known and widely used for many years. The principal advantages of a lithium soap grease have included high water resistance and ease of dispersion of the soap in all types of lubricating oil base stocks. While the lithium soaps used as thickening agents for these greases can be prepared by reaction of lithium hydroxide or other lithium base with conventional high molecular weight fatty acids, lithium hydroxy stearate and the lithium soaps of related hydroxy fatty acids have been particularly useful because of their great mechanical stability.

There are many fields of application of grease compositions where a high dropping point is required, as for example in the lubrication of traction motor bearings. Such traction motors are used to propel modern diesel locomotives. The engines of the diesel locomotives generate direct current which is then used to run traction motors which are geared directly to the driving axle and wheel assemblies in each truck of the locomotive. A single traction motor may contribute 200 horsepower, and constitute 1/10 or more of the total motor power of the locomotive. The bearings of these locomotives may be required to operate for periods of as much as three years without any maintenance, and temperatures as high as 250° F. can be reached in such bearings.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, a lithium hydroxy fatty acid grease having a dropping point in excess of 500° F. is prepared from a C_{12} to C_{24} hydroxy fatty acid and from a C_4 to C_{12} dicarboxylic acid using a particular sequence of steps that includes two stages of heating within relatively narrow ranges of temperature.

Although the preparation of lithium soap greases from a mixture of monocarboxylic acids and dicarboxylic acids is known in the art, the present invention provides a method for making greases of 500° F. or more dropping point directly from the carboxylic acids rather than by use of esters of the acids, as taught for example in U.S. Patent 2,898,296. U.S. Patent 2,940,930 also teaches that high dropping point greases can be prepared from mixtures of monocarboxylic and dicarboxylic acids. However, in preparing the greases described in that patent, it was necessary to also include a glycol. The presence of a glycol is undesirable because it renders the grease prone to oxidation and makes the water resistance of the grease undesirably low in some applications. The present invention makes possible the preparation of a grease from a combination of hydroxy fatty acid and dicarboxylic aliphatic acid without the necessity of incorporating a glycol.

The total soap content of the grease of the present invention will be in the range of from about 2 to 30 wt. percent and preferably from about 5 to 20 wt. percent. The proportion of hydroxy fatty acid to dicarboxylic acid will be in the range of about 0.5 to 0.8 mole of dicarboxylic acid per mole of hydroxy fatty acid. In the case of a grease prepared from 12-hydroxy stearic acid and azelaic acid, the highest dropping point grease is obtained when the mole ratio of azelaic acid to hydroxy stearic acid is within the narrow range of about 0.54 to 1 and about 0.6 to 1.

The hydroxy fatty acid employed in preparing the greases of this invention will have from about 12 to 24, or more usually about 16 to 20 carbon atoms, and will preferably be a hydroxy-stearic acid, e.g. 9-hydroxy, 10-hydroxy, or 12-hydroxy, stearic acid, more preferably the latter. Richinoleic acid, which is an unsaturated form of 12-hydroxystearic acid, having a double bond in the 9–10 position, can also be used.

The dicarboxylic acid used in the greases of this invention will have from 4 to 12 carbon atoms, preferably 6 to 10 carbon atoms. Such acids include succinic, glutaric, adipic, suberic, pimelic, azelaic, dodecanedioic, and sebacic acids. Sebacic acid and azelaic acid are preferred.

The lubricating oil base that is used in preparing the grease compositions of this invention can be any of the conventionally used mineral oils, synthetic hydrocarbon oils or synthetic ester oils. In general these lubricating oils will have a viscosity in the range of about 35 to 300 SUS at 210° F. Mineral lubricating oil base stocks used in preparing the greases can be any conventionally refined base stocks derived from paraffinic, naphthenic and mixed base crudes. Synthetic lubricating oils that can be used include esters of dibasic acids, such as di-2-ethylhexyl sebacate, esters of glycols such as a C_{13} oxo acid diester of tetraethylene glycol, or complex esters such as one formed from 1 mole of sebacic acid and 2 moles of tetraethylene glycol and 2 moles of 2-ethylhexanoic acid. Other synthetic oils that can be used include synthetic hydrocarbons such as alkyl benzenes, e.g. alkylate bottoms from the alkylation of benzene with tetrapropylene, or the copolymers of ethylene and propylene; silicon oils, e.g. ethyl phenyl polysiloxanes, methyl polysiloxanes, etc.; polyglycol oils, e.g. those obtained by condensing butyl alcohol with propylene oxide; carbonate esters, e.g. the product of reacting C_8 oxo alcohol with ethyl carbonate to form a half ester followed by reaction of the latter with tetraethylene glycol, etc. Other suitable synthetic oils include the polyphenyl ethers, e.g. those having from about 3 to 7 ether linkages and about 4 to 8 phenyl groups. (See U.S. Patent 3,424,678, column 3.)

In the process of the present invention, greases of high dropping point are prepared by a procedure that involves two separate heating stages. In the first stage, the hydroxy fatty acid and the dicarboxylic acid are dissolved with stirring at an elevated temperature, e.g. at about 180–210° F. in a portion of the base oil that is to be used in preparing the grease. Usually about 30 to 75% of the total amount of base oil is used in this step. Thereafter, a concentrated solution of lithium hydroxide in water is added slowly over a period of 1 to 2 hours, during which time the mixture is heated to a sufficiently high temperature, for example, about 290–310° F. to ensure the elimination of water. Then the temperature is further raised to at least 410° F. but no higher than about 430° F. The preferred temperature is 415–420° F. As soon as the grease temperature reaches 420° F. the

balance of the oil used in preparing the grease is added and the temperature of the grease is then rapidly brought down to about 220° F. Much of this reduction in temperature is brought about by the addition of the balance of the base oil which is normally at about ambient temperature. Additional rapid cooling is effected by circulating a cooling medium through the jacket of the kettle. There is no need to reduce the temperature below about 220° F., nor is it necessary to hold the temperature at this point for any particular length of time before proceeding to the second heating stage. In the second heating stage the mixture is reheated to a temperature of 350–375° F., and then cooled immediately to a temperature in the range of 220 to 240° F. The cooling to at least 240° F. is done as rapidly as possible to ensure the formation of a good balance of coarse and fine soap fibers. Then stirring is discontinued and the grease is allowed to gel for a number of hours, e.g. 8 to 16 hours at 220–240° F. Thereafter the grease is run through a conventional grease mill and cooled to room temperature. Suitable grease mills include the Morehouse mill, the Gaulin homogenizer, and the Charlotte mill.

The nature of this invention and the manner which it is practiced will be better understood when reference is made to the following examples which include preferred embodiments.

Example 1

A grease was prepared in accordance with this invention by charging to a grease kettle 70 grams (0.233 mole) of 12-hydroxy stearic acid, 24.13 grams (0.128 mole) of azelaic acid and 333.3 grams of base oil identified as LCT–20 base, which was a solvent refined and hydrofinished naphthenic distillate having a viscosity of 315 SUS at 100° F. and a V.I. of 67. The contents of the kettle were heated to 200–205° F. with stirring. After 20 minutes the acids were completely dissolved in the base oil. Then over a period of one hour there was added to the stirred mixture a concentrated solution of 21.9 grams (0.52 mole) of lithium hydroxide monohydrate in 160 milliliters of water. This amount of lithium hydroxide was 0.031 mole in excess of the amount theoretically required to neutralize the acids and was sufficient to give the finished grease a free alkali content of 0.1 to 0.2% by weight. After the addition of the lithium hydroxide, the temperature of the mixture was raised over a period of about 30 minutes to 300° F., where it was held for one hour to ensure the elimination of water. Then the temperature was further raised to 415–420° F. As soon as this temperature was reached, an additional 184 grams of the base oil and 316 grams of a paraffinic oil were added, these added portions of oil being at ambient temperature. The paraffinic oil was derived from a paraffinic distillate by phenol extraction and solvent dewaxing to +30° F. pour point and had a viscosity index of 75 and a viscosity of 155 SUS at 210° F. After the additional oil had been stirred in, the temperature of the grease was brought down to 220° F. in about 20 minutes. The contents of the kettle were then reheated to 350–375° F., and subsequently cooled to 220° F. over a period of one-half hour, at which point stirring of the mixture was discontinued and the grease was allowed to stand at 220° F. for 8 to 12 hours to cause gelation. Then the grease was milled in a Charlotte mill and cooled to room temperature. The final grease had a dropping point of 540° F. and a penetration of 264 ASTM units at 77° F. The yield of grease was 10.1%. As is well understood in the grease art, the total weight of acids used, expressed as a percentage of the total weight of finished grease, is referred to as the "yield."

Example 2

The procedure of Example 1 was repeated but the mole ratio of azelaic acid to 12-hydroxy stearic acid was varied in the range of 0.2 mole of azelaic acid per mole of hydroxy stearic acid to 0.75 mole of azelaic acid per mole of 12-hydroxy stearic acid. The dropping points and ASTM penetrations of the resulting greases were then determined. The results obtained are shown in Table I which follows:

TABLE I

Moles azelaic acid per mole 12-OH stearic acid	Dropping point, (° F.)	ASTM penetration at 77° F.
0.20	400	----
0.50	478	258
0.54	540	264
0.75	494	278

It will be noted that the highest dropping points were obtained when the mole ratio of azelaic acid to hydroxy stearic acid exceeded 0.5 to 1, a dropping point of 540° F. being obtained with a ratio of 0.54 mole of azelaic acid per mole of hydroxy stearic acid.

Comparative examples

Example 1 was again repeated using the same ratios of components as in Example 1 but varying the temperatures in the first stage and in the second stage. The dropping points of the greases thereby obtained were determined. The results are shown in Table II which follows.

TABLE II.—EFFECT OF TEMPERATURE OF HEATING

First stage	415–420	415–420	415–420	415–420	390	375
Second stage	325	350	375	400	375	415
Dropping point of grease, ° F	458	527	540	470	494	436
ASTM penetration, 77° F. worked 60 strokes	263	259	264	264	266	263

It will be noted from Table II that the dropping points of the greases exceeded 500° F only when the temperature of the first stage was held within the limits of 415–420° F. and the temperatures in the second stage were held within the limits of 350–375° F.

When Example I was again repeated, using a 415–420° F. temperature range for the first stage and omitting altogether the second stage of heating, the dropping point of the resulting grease was only 489° F.

It is to be noted that all of the grease compositions in Table II had the same total thickener content and very nearly the same consistency (ASTM penetration). Thus the variation in dropping points with change in preparation procedure is a valid comparison.

Various other additives may be incorporated into the grease compositions of this invention, as is understood by those skilled in this art. Such additives include, but are not limited to, dyes, antioxidants such as phenyl-alphanaphthylamine, rust inhibitors such as barium dinonyl naphthalene sulfonate, odor modifiers, tackiness agents, extreme pressure agents, and the like.

This invention is not to be limited to the specific examples given herein by way of illustration. Its scope is defined by the appended claims.

What is claimed is:

1. An improved process for preparing a lubricating grease of high dropping point, said grease comprising a major proportion of lubricating oil and from about 2 to about 30 weight percent of the lithium soaps of a mixture of a C_{12} to C_{24} hydroxy fatty acid and a C_4 to C_{12} aliphatic dicarboxylic acid, which includes the steps of converting said mixture of acids to the lithium soaps in a portion of said lubricating oil, thereafter increasing the temperature to about 410–430° F., adding the remaining portion of lubricating oil, rapidly lowering the tempera-

ture to a point not in excess of about 220° F., thereafter reheating the mixture to a range of about 350–375° F., then rapidly reducing the temperature to a range of about 220 to 240° F., and holding the resulting grease at said latter temperature for a sufficient period of time to cause gelation, wherein the ratio of said acids is within the range of 0.5 to about 0.8 mole of dicarboxylic acid per mole of hydroxy fatty acid.

2. Process as defined by claim 1 wherein said acids comprise a mixture of a C_6 to C_{10} dicarboxylic acid and a C_{16} to C_{20} hydroxy fatty acid.

3. Process as defined by claim 1 wherein said hydroxy fatty acid is 12-hydroxy stearic acid.

4. Process as defined by claim 1 wherein said dicarboxylic acid is azelaic acid.

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