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LITHIUM GREASES

John Greenwood, Didcot, and Ernest Augustus Saxon-Napier, Reading, England, assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to a process for preparing greases derived from a base lubricating oil and a lithium soap of a hydroxy fatty acid, and which contains an aliphatic polyhydroxy structure modifier, and particularly relates to such a process in which the lubricity of such a grease is improved by incorporating the said polyhydroxy structure modifier into a grease-forming composition at the maximum temperature of the constituents during manufacture.

A known method of manufacturing greases using lithium hydroxy soaps as a gelling agent, is to incorporate the lithium soaps of hydroxy fatty acids (or constituents which produce such soaps) in a base lubricating oil, which mixture is then heated to a temperature of about 180–220° F. whereby the mixture is dehydrated. The mixture is then further heated to a maximum temperature in the range of about 380–420° F. The composition is held at the maximum temperature for as short a time as possible to ensure homogeneous heating, usually about 10 minutes with stirring and then cooled to a setting temperature, i.e. at a temperature at which solid particles first appear in the grease-forming composition. During cooling, and at a temperature usually, but not necessarily, below the setting temperature, the grease-forming composition passes through a so-called "transition-temperature," which point is characterized by the evolution of heat from the cooling composition. The transition temperature can vary from one type of soap to another, and may in some instances be above the maximum grease-forming temperature. After passing through the transition temperature, it is desirable to hold the grease at an elevated temperature for an extended period of time to improve the final grease structure. This so-called "heat-soak" preferably occurs at a temperature below the transition temperature, and may range up to about 75° F. below the transition temperature, and may extend for a period of time of about 10 minutes to 4 hours.

It has previously been proposed that such a grease having an improved structure may be obtained by incorporating a glyceride in the constituents, from which the acid constituent of the grease-forming soap is derived. During manufacture the glyceride is hydrolyzed, resulting in a glycerol content of 1.3 to 1.5 weight percent based on the total composition. While such a procedure may result in a grease of somewhat improved structure, such greases derived from glycerides and manufactured according to the procedure hereinbefore described are not always successful in meeting present-day high duty lubricating requirements.

It has now been discovered that the lubricating properties of greases of the type hereinbefore described, i.e. derived from soaps of lithium soaps of hydroxy-substituted fatty acids, have their lubricating properties unexpectedly improved by the addition of a free aliphatic polyhydroxy structure modifying agent at a particular stage of grease manufacture, namely at or near the maximum temperature reached during the grease-manufacturing process as hereinbefore described. Thus the structure-modifying agent is preferably added at a temperature within the range 375–425° F.

It is a preferred feature of this invention that oxidation inhibiting compounds which are well-known constituents of grease compositions, should also be added at or near the aforesaid maximum temperature of the grease-forming constituents and particularly before the structure modifying agent. If the anti-oxidant is added at a lower temperature, e.g. during the cooling of the grease or after the structure modifying agent, the final grease is unexpectedly deficient in lubricating properties.

Particularly useful greases according to this invention are obtained by incorporating a small proportion of lead or zinc naphthenate therein in addition to the polyhydroxy structure modifying agent. Proportions of the said naphthenate preferably range from 0.1 to 6%, preferably 1% to 2.5% by weight, based on the total composition. Besides improving the corrosion-resistance of the greases in which they are incorporated, it appears that greases may be obtained which have equivalent lubricating properties but which contain somewhat smaller proportions of the poly-hydroxy structure-modifying agent, than are necessary in the absence of the said naphthenates.

Greases prepared according to this invention, while showing improved lubricating properties, also display lower transition points during cooling of the grease-forming mixtures.

Aliphatic structure modifiers used in the process of this invention include glycols, polyglycols, e.g. polyethylene or propylene glycols, the polyglycols preferably having a molecular weight between about 450 and 650, glycerol, pentaerythritol, hexane 2,5 diol, and partial esters of sorbitol, e.g. sorbitan mono-oleate or stearate. The proportions of polyhydroxy compound used is preferably between 1% and 4% by weight, based on the total composition. In the case of glycerol, particularly useful results are obtained when the glycerol is present in proportion of about 2%. It is an essential feature of the invention that the free polyhydroxy compound is incorporated in the grease-forming composition at or near the maximum temperature.

Anti-oxidant compounds incorporated in the grease compositions of this invention are a usual and well-known class of compounds for grease compositions, particularly nitrogen and/or phosphorus-containing compounds and phenolic compounds, and include phenothiazine, alkyl-substituted phenothiazine phenyl-naphthylamine, alkyl-substituted phenols, including 2,6'- and 2,4,6-substituted phenols for instance 2,6 tert. butyl 4 methyl phenol substituted diphenylamines, for instance di-octyl phenylamine, and alkyl-substituted bisphenols, metal salts of di-alkyl dithio dithiophosphate including cadmium and zinc salts thereof and metal dithiocarbamates. These compounds incorporated in the grease-forming composition according to this invention enables the improved lubricating properties donated by the structure-modifying compounds to be preserved, often with a smaller proportion of polyhydroxy compound than would otherwise be necessary. It is preferred that the anti-oxidant compound is added before the polyhydroxy structure modifier is added.

The lithium soaps used as gelling-agents in the composition of this invention include soaps of hydroxy-substituted C_{12}–C_{24} fatty acid, for instance lithium 12–OH stearate. The soap is preferably formed during heating by interaction between lithium hydroxide and the free acid.

A typical manner of manufacture according to this invention is to incorporate a C_{12}–C_{24} hydroxy-substituted fatty acid in a major proportion of the lubricating oil, e.g. a mineral oil of viscosity 35–200 SUS/210° F., although synthetic oils may be used, and heat to a temperature of about 180° F., thereafter slowly adding lithium hydroxide dissolved in water in a total amount to form a soap with the fatty acid. The amount of fatty acid added in the first instance should be sufficient to form the desired grease-consistency in the final composition when it is completely saponified. The actual amount of fatty acid used will therefore depend on the particular acid used, the nature of the base oil, and the use for which the grease is in-

tended. As a general guide however, from 4% to 25% by weight based on the lubricating oil, may be incorporated. After the lithium hydroxide is added, the mixture is heated to 300° F. with stirring for a period of time until the water present has been removed. The mixture is then further heated to a temperature of about 375–425° F., and the anti-oxidant compound, preferably dissolved in the remainder of the base oil (e.g. in about 2% to 6% of the oil) is added, followed by the addition with stirring of the aliphatic polyhydroxy structure-modifying agent in proportions preferably of the order of 1% to 4% by weight. The mixture is then cooled as quickly as possible to about 375° F., and then further cooled at a slower rate, to reach about 315° F. The grease mixture is then held at this temperature for a period of time about 15 minutes to 2 hours, and then cooled to 140° F. The mixture is continuously stirred while cooling. The grease is homogenized, for instance in a colloid mill, and deaerated.

Particular embodiments of this invention are hereinafter described.

Four greases were prepared, comprising a mineral base oil thickened to a grease consistency with lithium hydroxy stearate, and containing phenyl β-naphthylamine as an anti-oxidant. Grease "A" contained no structure-modifying agent. In Grease "B" the lithium soap was derived from a glyceride of 12–OH stearic acid hydrolyzed at a low temperature to produce the fatty acid. Grease "C" was prepared according to this invention, containing 2% by weight of glycerol as a structure-modifying agent added to the grease-forming composition at the maximum temperature, e.g. 400° C. Grease "D" was similar to Grease "C," except that the anti-oxidant was added at a lower temperature after the glycerol.

Grease A

Grease A was prepared from a composition consisting of:

	Weight Percent
Lithium hydroxide monohydrate	2.1
12–OH stearic acid	13.3
Phenyl β-naphthylamine	0.9
Mineral oil viscosity 110 cs./100° F.	83.7

The 12–OH stearic acid was incorporated in 96% of the total base oil, heated to 180° F., at which temperature an aqueous solution of lithium hydroxide was added. The mixture was dehydrated at 220° F., and then heated to 400° F. The mixture was then cooled to 375° F., during which time the anti-oxidant was added dissolved in the remaining 4% of the base oil, and then further cooled to 315° F., and held at this temperature for 2 hours. The gelled mixture was then further cooled to 140° F., and milled in a colloid mill with 0.006" to 0.015' mill clearance, and then deaerated. The composition was continuously stirred during manufacture.

Grease B

Grease B was prepared in a similar manner to Grease A, except that the fatty acid was derived from 12.8 wt. percent of the glyceride of 12–OH stearic acid. The glyceride was dissolved in its own weight of oil, saponified with the lithium monohydrate, 25% of the total base oil added, dehydrated at 300° F., the remainder of the base oil added, (less 4%), heated to 400° F., cooled to 315° F., the anti-oxidant added in 4% of the oil solution and the grease finished as Grease A. The final grease contained 1.3% of glycerol.

Grease C

Grease C was prepared in a similar way to Grease A, except that the anti-oxidant was added at the maximum temperature of 400° F., after which 2% of glycerol as a structure-modifying agent was also added while the mixture was still at the same high temperature.

Grease D

Grease D was also prepared in a similar way to Grease C, except that the anti-oxidant was added to the composition after the glycerol, at a temperature of 320° F., i.e. while the grease-forming mixture was cooling.

The above four greases were tested in the Hoffman High Speed Rig.

TABLE I

Grease	Penetration (×60) mm./10, ASTM D217	Transition Point, ° F.	Hoffman High Speed Rig Test	
			Hours Run	Cage Wear, inches
A	238	400	500	0.021
B	242	366	168	0.016
C [1]	223	344	500	NIL
D [1]	289	330	500	0.006

[1] Prepared according to the invention.

It will be observed from Table I that the lubricating properties of greases as exemplified by the cage wear are greatly improved when a polyhydroxy structure modifier is included in the formulations when the latter are at the maximum temperature, and also that the best results both from yield and anti-wear properties are obtained when the anti-oxidant and the polyhydroxy compound are both added when the grease-forming composition is at the maximum temperature, as shown by Grease "C."

Greases of enhanced corrosion resistance may be obtained according to this invention by incorporating small proportions up to 5%, preferably 0.5 to 2.5% by weight, of zinc or lead naphthenate. In such instances greases of comparable structure and properties may be obtained with proportions of polyhydroxy structure-modifiers substantially reduced over the proportions used in the absence of the naphthenates. Anti-wear additive compounds may also be incorporated in the composition of this invention, particularly molybdenum disulphide.

What is claimed is:

1. A process for preparing a lubricating grease composition which comprises:
   (*a*) incorporating a grease-forming amount of lithium soap of C_{12}–C_{24} hydroxy fatty acid in a lubricating oil vehicle to thereby form a mixture,
   (*b*) heating said mixture for a period of time sufficient to cause dehydration,
   (*c*) further heating said mixture to a maximum temperature of about 375–425° F.,
   (*d*) adding from 1–4 weight percent of glycerol, based on the total weight of said grease composition, to said mixture at about said maximum temperature, and
   (*e*) cooling said mixture to form said grease composition.

2. A process as defined in claim 1 wherein an anti-oxidant for lubricating greases is also added to said mixture at about said maximum temperature.

3. A process as defined in claim 2 wherein said anti-oxidant is added prior to said glycerol.

4. A process as defined in claim 3 wherein said anti-oxidant is phenyl beta naphthylamine.

5. A process as defined in claim 4 wherein from 0.1 to 6.0 weight percent of a material selected from the group consisting of lead naphthenate and zinc naphthenate is also added to said mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 23,243	Bondi	June 20, 1950
2,449,312	Murray et al.	Sept. 14, 1948
2,450,221	Ashburn et al.	Sept. 28, 1948
2,470,965	Woods et al.	May 24, 1949
2,487,081	Swenson	Nov. 8, 1949
2,666,033	Dilworth et al.	June 12, 1954
2,812,306	Liehe	Nov. 5, 1957
2,895,914	Kern et al.	July 21, 1959