

PATENT SPECIFICATION

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 (72) Inventor GARY LORVIN HARTING



(54) LITHIUM SOAP GREASE CONTAINING MONOLITHIUM BORATE

(71) We, EXXON RESEARCH & ENGINEERING COMPANY, formerly known as Esso Research and Engineering Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a modified lithium soap grease of premium quality with outstanding properties which include a high dropping point, excellent oxidation stability, long lubrication life and water resistance.

Invention is an improvement in or modification of the invention described in Specification No. 1,364,648, filed November 12, 1971.

Lithium greases have been known and widely used for many years. The lithium soaps that are used as thickening agents for these greases are ordinarily prepared by reaction of lithium hydroxide or other suitable lithium base with a conventional high molecular weight acid or acids. The principal advantages of lithium greases have been high water resistance and ease of dispersion of the soaps in all types of lubricating oil base stocks. Particularly useful have been greases prepared from lithium hydroxystearate, since the soaps of the hydroxystearic acids and related hydroxy fatty acids have been found to be more mechanically stable than the corresponding soaps of the conventional fatty acids.

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. 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.

It has already been taught in U.S. Patent 2,940,930 that high dropping point greases (500° F. or greater) 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 high dropping point greases from hydroxy fatty acids without the necessity of incorporating a glycol.

While U.S. Patents 3,223,633 and 3,223,624 teach the preparation of high dropping point greases from a 3-component mixture of acids, the presence of a C₂ to C₄ fatty acid salt, which is an essential component of those greases, is frequently undesirable because of the tendency of such greases to undergo surface hardening on standing.

According to the present invention a lubricating grease composition of high dropping point comprises a major proportion of a lubricating oil and from 2 to 30 wt. % of a thickener system whose essential constituents include a lithium soap of a C₁₂ to C₂₄ hydroxy fatty acid (usually about 16 to 20 carbon atoms, and will preferably be a hydroxystearic acid, e.g., 9-hydroxy, 10-hydroxy, or 12-hydroxystearic acid, more preferably the latter), and a monolithium salt of boric acid; wherein there are from 3 to 100 parts by wt.

[Price 25p]

of hydroxy fatty acid per part by wt. boric acid. An unsaturated form of 12-hydroxystearic acid, such as ricinoleic acid having a double bond in the 9—10 position, can be used as the C₁₂ to C₂₄ acid. Other hydroxy fatty acids include 12-hydroxybehenic acid and 10-hydroxypalmitic acid.

Preferably the thickener system includes a third essential component, viz., a lithium salt of a second hydroxycarboxylic acid. Said second acid will be one having an OH group attached to a carbon atom that is not more than 6 carbon atoms removed from the carboxyl group. This second acid must also have from 3 to 14 carbon atoms. It can be either an aliphatic acid such as lactic acid, 6-hydroxydecanoic acid, 3-hydroxybutanoic acid, 1-hydroxycaproic acid, 4-hydroxybutanoic acid, or 6-hydroxy- α -hydroxystearic acid; or an aromatic acid such as parahydroxybenzoic acid, salicylic acid, 2-hydroxy-4-hexylbenzoic acid, metahydroxybenzoic acid, 2,5-dihydroxybenzoic acid (gentisic acid), 2,6-dihydroxybenzoic acid (gamma resorcylic acid), 4-hydroxy-4-methoxybenzoic acid; or a hydroxyaromatic aliphatic acid such as orthohydroxyphenyl, metahydroxyphenyl, or parahydroxyphenyl acetic acid. A cycloaliphatic hydroxy acid such as hydroxycyclopentyl carboxylic acid or hydroxynaphtheneic acid could also be used. Particularly useful hydroxy acids are lactic acid, salicylic acid, and parahydroxybenzoic acid.

In place of the free hydroxy acid of the latter type when preparing the grease, one can use a lower alcohol ester, e.g., the methyl, ethyl, or propyl, isopropyl, or sec-butyl ester of the acid, e.g., methyl salicylate, to give a better dispersion when the salt is insoluble. The amount of lithium salt of the second hydroxy acid will range from about 0.1 to about 10 wt. % of the finished grease, or preferably from about 0.2 to about 5 wt. %. The monolithium salt or the dilithium salt of the second hydroxy acid can be used, but the dilithium salt is preferred.

The total soap and salt content of the grease will be in the range of from 2 to 30 wt. % and preferably 5 to 20 wt. %. The proportion of the C₁₂ to C₂₄ hydroxy fatty acid to boric acid will be in the range of a weight ratio (calculated as free acids) of 3 to 100 parts, or more usually 5 to 80 parts, of hydroxy fatty acid per part by weight of boric acid. There will be a weight ratio (calculated as free acids) of 0.1 to 10, or more usually 0.5 to 5 parts of said second hydroxycarboxylic acid per part by weight of boric acid in the case of the greases made from 3 acid components.

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, and will generally have a viscosity within the range of about 35 to 200 SUS at 210° F. Synthetic lubricating oils that can be used include esters of dibasic acids such as di-2-ethylhexyl sebacate, esters of glycols such as the C₁₃ oxo acid diester of tetraethylene glycol, or complex esters such as a complex ester formed by reacting 1 mole of sebacic acid with 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; silicone oils, e.g., ethylphenyl polysiloxanes, or methyl polysiloxanes; polyglycol oils, e.g., those obtained by condensing butyl alcohol with propylene oxide; carbonate esters, e.g., the product of reacting C₈ oxo alcohol with ethyl carbonate to form a half ester followed by reaction of the latter with tetraethylene glycol. 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).

The greases can be prepared by co-neutralizing all three types of acid, or alternatively by first neutralizing the boric acid and hydroxy fatty acid together and then forming the lithium salt of the second hydroxycarboxylic acid.

The following non-limitative examples, which include preferred embodiments, are presented to illustrate the preparation and various characteristics of greases manufactured according to this invention. Comparative examples are also included to show that inferior results are obtained if boric acid is omitted or if the boric acid is neutralized beyond the monolithium salt stage.

EXAMPLE I.

(Including Comparative Greases).

A grease designated grease A was prepared using as the thickener system a combination of lithium 12-hydroxystearate and monolithium borate. The base oil used in preparing this grease was a solvent-refined mid-continent lubricating oil distillate known as Solvent 450 Neutral, having a viscosity at 100° F. of about 450 SUS. The 12-hydroxystearic acid was added to a portion of the base oil (about $\frac{1}{2}$ of the total oil used in the complete grease) and the mixture was heated to a temperature sufficiently high to melt the 12-hydroxystearic acid, this temperature being about 180° F. to 190° F. Then the boric acid and the lithium hydroxide monohydrate were added as an aqueous solution, and the resulting mixture was stirred and heated to a final temperature of about 380° F. to 390° F. Then the remaining portion of the base oil was added and the mixture was

cooled to ambient temperature and milled in a conventional grease mill. A comparative grease corresponding to A but omitting the boric acid was also prepared.

- 5 Two additional greases were prepared using in each case the same proportion of 12-hydroxystearic acid and boric acid to base oil as in grease A but increasing the amount of

lithium hydroxide monohydrate so as to form dilithium borate and trilithium borate instead of monolithium borate.

Each of the greases thus prepared was measured for dropping point and for ASTM penetration at 77° F. The composition of the greases and the inspections are shown in Table I which follows:

TABLE I

Composition, Grams	Comparative Greases			
	Grease of Invention	No Boric Acid	Dilithium Borate	Trilithium Borate
	Monolithium Borate			
	A	1	2	3
LiOH.H ₂ O	12.6	7.0	17.2	23.8
12-Hydroxystearic Acid	50	50	50	50
Boric Acid	8.3	0	8.3	8.3
Base Oil	433.1	433.1	433.1	433.1
Inspections				
Dropping Point, °F.	484	407	419	403
ASTM Penetration at 77°F., 60 Strokes	231	239	218	220

The data in Table I lead to the following observations.

- 20 Comparison of grease A with grease 1 shows that monolithium borate provides a grease of high dropping point and desirable consistency.

- 25 The data for greases 2 and 3 indicate that when the ratio of lithium to boric acid is increased beyond the proportion needed to form the monolithium borate the desired improvement in dropping point is not obtained.

30 EXAMPLE 2.

- Two greases were prepared using as the thickener system a combination of dilithium calicylate, lithium 12-hydroxystearate and monolithium borate, the proportions of the thickener components being varied as between two greases. The base oil used in preparing these greases was a solvent refined mid-continent lubricating oil distillate known as Solvent 600 Neutral, having a viscosity at 100° F. of about 600 SUS. Methyl salicylate and 12-hydroxystearic acid were added to a portion of the base oil and the mixture was heated. After it was observed that the 12-hydroxystearic acid had melted, the temperature being then about 180° F. to 190° F., all of the lithium hydroxide that was to be used in forming the various lithium salts was

added in the form of a 10% aqueous solution to which had also been added the boric acid that was to be used in making the grease. The resulting mixture was stirred and heated to a final temperature of about 380° F. to 390° F. Then the remaining portion of the base oil was added and the mixture was cooled to about 250° F. at which point, an antioxidant and other components of the grease such as rust inhibitors were incorporated. The grease was then milled in a conventional grease mill.

By the same procedure a third grease was prepared using as a thickener system a combination of lithium 12-hydroxystearate and monolithium borate only.

COMPARATIVE EXAMPLE.

Using the same procedure as in Example 2, two comparative greases were prepared in which in one case the boric acid was omitted and in the second case both the boric acid and methyl salicylate were omitted. In each instance the corresponding quantity of lithium hydroxide needed to form the soap or salt of the omitted component was also omitted. Each of the greases prepared as in Example 2 and in the Comparative Example was measured for dropping point and for ASTM penetration at 77° F. The composition of each of the greases and the inspections are shown in Table II which follows.

TABLE II

Composition, Weight %	Greases of Invention			Comparative Greases	
	M	N	O	Y	Z
LiOH.H ₂ O	4.0	1.9	2.5	2.9	1.8
12-Hydroxystearic Acid	12.9	10.4	12.9	11.5	12.9
Boric Acid	1.1	0.5	1.1	—	—
Methyl Salicylate	2.7	0.5	—	2.5	—
Base Oil	78.3	84.7	82.5	81.1	85.3
Phenyl Alpha Naphthylamine	1.0	1.0	1.0	1.0	—
Na-Sul-BSN	—	1.0	—	1.0	—
Inspections					
Dropping Point, °F.	500+	500+	437	415	405
ASTM Penetration @77°F.					
Unworked	252	275	262	217	261
60 Strokes	261	280	255	240	250
10,000 Strokes	293	299	291	243	277

5 The phenyl alpha naphthylamine referred to was used as an antioxidant. The Na-Sul-BSN is a trademarked product which serves as a rust inhibitor; it is a 50 wt. % concentrate, in a light mineral oil, of a neutral barium salt of dinonyl naphthalene sulfonic acid derived from naphthalene alkylated with tripropylene.

10 Referring to the date in Table II, comparison of grease O with grease Z and with grease M shows that incorporation of monolithium borate into a lithium hydroxystearate grease increases the dropping point by a useful amount. However, even greater increase in dropping point results when lithium salicylate is also used. Comparison of greases Y and Z shows that incorporation of the lithium salicylate without the monolithium borate does not improve the dropping point significantly.

25 Various other conventional additives can be incorporated into the grease compositions of this invention, as is understood by those skilled in the art. Such additives include antioxidants, rust inhibitors, tackiness agents, odor modifiers, dyes, and extreme pressure agents.

WHAT WE CLAIM IS:—

30 1. A lubricating grease composition of high dropping point which comprises a major proportion of a lubricating oil and from 2 to 30

wt. % of a thickener system whose essential components include a lithium soap of a C₁₂ to C₂₄ hydroxy fatty acid and a monolithium salt of boric acid, wherein there are from 3 to 100 parts by weight of hydroxy fatty acid per part by weight of boric acid. 35

2. Composition as claimed in claim 1, wherein the thickener system also includes as a third essential component a lithium salt of a second hydroxycarboxylic acid of from 3 to 14 carbon atoms, wherein the hydroxy group is attached to a carbon atom not more than 6 carbon atoms removed from the carboxyl group, and wherein there is a weight ratio of from 0.1 to 10 parts of said second hydroxycarboxylic acid per part of boric acid. 40 45

3. Grease composition as claimed in claim 2, wherein said second hydroxycarboxylic acid is salicylic acid. 50

4. Grease composition as claimed in claim 2, wherein said second hydroxycarboxylic acid is lactic acid.

5. Grease composition as claimed in claim 2 wherein said second hydroxycarboxylic acid is parahydroxybenzoic acid. 55

6. Grease composition as claimed in any preceding claim, said hydroxy fatty acid is 12-hydroxystearic acid. 60

7. Grease composition as claimed in any preceding claim, and substantially as herein described.



TABLE II

Composition, Weight %	Greases of Invention			Comparative Greases	
	M	N	O	Y	Z
LiOH.H ₂ O	4.0	1.9	2.5	2.9	1.8
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Boric Acid	1.1	0.5	1.1	—	—
Methyl Salicylate	2.7	0.5	—	2.5	—
Base Oil	78.3	84.7	82.5	81.1	85.3
Phenyl Alpha Naphthylamine	1.0	1.0	1.0	1.0	—
Na-Sul-BSN	—	1.0	—	1.0	—
Inspections					
Dropping Point, °F.	500 ⁺	500 ⁺	437	415	405
ASTM Penetration @77 °F.					
Unworked	252	275	262	217	261
60 Strokes	261	280	255	240	250
10,000 Strokes	293	299	291	243	277

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30 WHAT WE CLAIM IS:—

1. A lubricating grease composition of high dropping point which comprises a major proportion of a lubricating oil and from 2 to 30

wt. % of a thickener system whose essential components include a lithium soap of a C₁₂ to C₂₄ hydroxy fatty acid and a monolithium salt of boric acid, wherein there are from 3 to 100 parts by weight of hydroxy fatty acid per part by weight of boric acid. 35

2. Composition as claimed in claim 1, wherein the thickener system also includes as a third essential component a lithium salt of a second hydroxycarboxylic acid of from 3 to 14 carbon atoms, wherein the hydroxy group is attached to a carbon atom not more than 6 carbon atoms removed from the carboxyl group, and wherein there is a weight ratio of from 0.1 to 10 parts of said second hydroxycarboxylic acid per part of boric acid. 40 45

3. Grease composition as claimed in claim 2, wherein said second hydroxycarboxylic acid is salicylic acid. 50

4. Grease composition as claimed in claim 2, wherein said second hydroxycarboxylic acid is lactic acid.

5. Grease composition as claimed in claim 2 wherein said second hydroxycarboxylic acid is parahydroxybenzoic acid. 55

6. Grease composition as claimed in any preceding claim, said hydroxy fatty acid is 12-hydroxystearic acid. 60

7. Grease composition as claimed in any preceding claim, and substantially as herein described.



8. Grease composition as claimed in claim 1, and substantially as herein described with reference to Example 1 or Example 2.

K. J. VERYARD,
15, Suffolk Street, London, S.W.1,
Agent for the Applicants.

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