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LUBRICATING GREASE COMPOSITION AND PREPARATION

The present invention relates to a lubricating grease composition and preparation thereof, being more especially concerned with lubricating greases having improved consistency and homogeneity and low noise characteristics.

The lubricating grease types with which the invention is concerned comprise a major proportion of a lubricating base oil and a minor proportion of a simple soap or a complex soap thickener or of an organic thickener or inorganic clay thickener, such grease types include but are not limited to lithium simple and complex soap greases, calcium simple and complex soap greases, sodium simple and complex greases, aluminium simple and complex greases, barium simple and complex greases; as well as polyurea greases, organo-clay greases and bentonite clay/swelling-clay type thickeners.

It is an object of the present invention to provide a grease in which the thickener is of improved, e.g. smaller, more uniform, particle size. Such an improved structure will endow most grease types with e.g. improved consistency and useful life-time, and reduced oil separation. Although of general relevance, such an improved thickener is of especial advantage in lithium simple and complex soap greases.

As an example, lithium complex soap greases have found a major use as greases for bearings, particularly sealed bearings e.g. in automobiles and electrical appliances. Sealed bearing greases must meet numerous performance requirements including extended bearing life, high temperature performance, high dropping point; and defined requirements relating to oil separation, oxidation stability, fretting wear protection and low noise. However, although offering long service and high temperature benefits, such greases often suffer from generally higher noise characteristics than a lithium simple grease.

It is a further object of the present invention to provide a lubricating grease in general, but more especially a lithium complex grease, having reduced noise characteristics.



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In accordance with one aspect of the present invention there is provided a method of preparing a lubricating grease composition having a major proportion of lubricating base oil and a minor proportion of a simple soap or a complex soap thickener system, or of an organic thickener system or inorganic clay thickener system; which method includes the steps of:

(a) agitating and heating the soap-forming or other grease-thickening constituent(s) with at least a portion of the lubricating base oil in a closed reaction vessel over a temperature range and for a period of time sufficient to form a soap or other thickener system,

(b) cycling at least a portion of the contents of the reaction vessel, during at least the initial stage of the soap-forming, or other thickening, period, one or more times round a pressure-ventable closed processing loop including (i) the said agitating and heating in the reaction vessel and (ii) shearing the forming soap, or other thickener, in mechanical shearing means.

It is much preferred to conduct the cycling step (b) more than once during the said initial stage; and very preferably it is conducted over substantially the full soap-forming, or other thickening, period. Preferably, too, substantially all of the contents of the reaction vessel are cycled in at least one of the cycles of step (b); and, more preferably, in substantially all cycles.

The mechanical shearing is very preferably conducted with a shearing/milling/grinding gap of between 50 μm and 2000 μm , especially from 50 μm to 500 μm , more especially 100 μm to 500 μm . Suitably the mechanical shearing may be conducted employing one of the SUPRATON® machines e.g. the S400 model commercially available from Krupp Industrietechnik GmbH, Grevenbroich, Germany. Gaps between stator and rotor are set within the above ranges and, very preferably, reaction mix from the reactor is fed such that the dwell period of the material in the grinding gap is as extended as possible.

The following description relates to soaps and soap-forming, but is relevant to, and does not exclude, other types of thickening as referred to above.

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In the reaction vessel (grease-making kettle) itself the soap-forming constituents are heated over a continuing temperature gradient and agitated (i.e. thoroughly mixed, for example by means of a double-motion agitator) both initially and upon each return from shearing. The combination of the steps (a) and (b) of the process of the invention permits the generation of an extremely large and active contact surface between reactants with slow evaporation of water. As a result crystallization occurs such that the soap structure formed has, among other properties, a small size and a high measure of noise-absorption.

The invention thus provides a means of greatly decreasing that portion of the noise-causing characteristics of a grease which are due to the internal soap crystal structure *per se*. It is known that externally introduced contaminants will increase the noise rating of a grease, for example, reaction components contaminated prior to or during manufacture. Therefore, it is highly preferred in the process of the present invention to employ components in as impurity-free form as possible, such as by filtering them in liquid form through break-proof filter systems. In this way noise level of the grease product is still further decreased. However, the essence of the present invention is a significant reduction in noise due to the internal soap crystal structure; and it is achieved by the controlled crystallisation which occurs during the saponification stage of the process of the invention.

A wide variety of lubricating base oils can be employed in the process and grease compositions of the present invention. Thus, the lubricating oil base can be any of the conventionally used mineral oils, synthetic hydrocarbon oils or synthetic ester oils, or mixtures thereof depending upon the particular grease being prepared. In general these lubricating oils will have a viscosity in the range of about 5 to about 400 cSt at 40°C, although typical applications will require an oil having a viscosity ranging from about 10 to about 200 cSt at 40°C. 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 glycols such as a C₁₃ 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 polyalphaolefins; alkyl benzenes, e.g., alkylate bottoms from the alkylation of benzene with tetrapropylene, or the copolymers of ethylene and propylene; silicone 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 C₈

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.

5 For lithium complex soap greases, preferred thickeners contain two, more preferably, three lithium components. The first may be a lithium soap of at least one, hydroxy fatty acid, preferably C_{12} to C_{29} . The second may be selected from a lithium compound of (i) a C_2 to C_{12} aliphatic or cycloaliphatic dicarboxylic acid (or C_1 to C_{10} , such as C_1 to C_4 , alkyl ester thereof); or (ii) of a C_3 to C_{24} hydroxy
10 carboxylic acid (or C_1 to C_{10} , such as C_1 to C_4 , alkyl ester thereof) which has the hydroxy group separated from the carboxyl group by six or less carbon atoms; or a mixture thereof. The third component, which is very preferably present, is a lithium salt of boric acid.

Preferred hydroxy fatty acids include hydroxystearic, hydroxy-ricinoleic,
15 hydroxybehenic and hydroxypalmitic. Especially preferred is 12-hydroxystearic acid. The second lithium compound is preferably a C_6 to C_{10} aliphatic dicarboxylic acid, more preferably azelaic or sebacic acids, especially azelaic acid, or said ester of any of these. The C_3 to C_{24} hydroxycarboxylic acid is preferably lactic acid, salicylic acid or other hydroxy-benzoic acid, more preferably salicylic acid or
20 a said ester of any of these. The amount of lithium soap complex thickeners is very preferably from 5 to 20 wt.%, based on grease. The weight ratio of hydroxy fatty acid to aliphatic dicarboxylic acid and/or hydroxy-carboxylic acid is preferably from 10:0.5 to 10:15, very preferably 10:1.5 to 10:6. The weight ratio of boric acid to the dicarboxylic and/or hydroxy carboxylic acid will preferably be from 1:5 to
25 1:20 very preferably 1:10 to 1:15.

Lubricating greases formed in accordance with the invention, both as broadly and more specifically defined herein, may have a noise level of not above 3.5 units when measured by the SKF "BEQUIET" test rig referred to herein. A level of 2.0 to 3.0 units is one achievable range.

30 Such a lubricating grease composition may include (i) a major amount by weight of a lubricating base oil; (ii) from 2 to 30 wt.%, preferably 2 to 20 wt.%, of a lithium complex soap thickener; and (iii) 0 to 10 wt.%,

suitably 0 to 5 wt.%, of conventional additives; and having (a) a noise level below 3.5 units when measured as herein referred to.

Such a lithium complex grease will normally have a dropping point (ASTM D 566-87) of at least 270°C, usually at least 290°C.

The following Examples are given as non-limitative illustration of aspects of the present invention.

EXAMPLE 1

A lithium complex grease was made employing a paraffinic base oil of 100 to 120 cSt at 40°C, 12-hydroxystearic acid, lithium hydroxide, methyl salicylate and boric acid, in proportions approximating to those conventionally employed. The base oil and pre-solutions of components were filtered to < 50 µm and < 25 µm for water-soluble and oil-soluble components respectively (although in general, it will be found more advantageous to employ filters of the same mesh size, and in the order of about 10 µm).

The 12-hydroxystearic acid and a minor, solubilising, quantity of the base oil were heated to approximately 85°C. The pre-solution was filtered and pumped into a closed kettle.

The methyl salicylate was added to the closed kettle at approximately 80°C and heating commenced. When the temperature reached about 95°C, a pre-made aqueous solution (at about 95°C) of lithium hydroxide and boric acid was added to the closed vessel. The reactor contents were kept thoroughly agitated throughout the manufacture. As from the time the LiOH was added, substantially the entire reaction mixture was fed around a closed ventable loop which included a shearing stage at less than 500 µm stator/rotor slit width in a SUPRATON® Mill referred to herein. (The term "shearing" as used herein encompasses shearing, grinding, milling and homogenising). The cycling was continued in a substantially constant manner.

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Heating was continued to 140°C, whereupon a further portion of the base oil was added to the kettle. Heating was continued to approximately 190°C, whilst continuing the circulation of mix through the mill. At that point the cycling was stopped, the kettle cooled, and conventional corrosion inhibitor and antioxidant were added in a further amount of the base oil and blended in.

Finally, the remainder of the base oil was added and the whole blended to produce a final grease having a penetration of approximately mid-NLGI 3 range, 220-250 units.

EXAMPLE 2

The noise characteristics of three lithium complex greases prepared in accordance with the procedure of Example 1 were compared with those of (A) the grease of Samples 4 and 12 described in WO 95/35355 and (B) a commercially available polyurea grease known to exhibit low noise properties.

The test was made employing the commercially available SKF "BEQUIET" test rig MVH 90B, obtainable from the SKF Company, Sweden. The noise level results obtained by this method, so-called Anderometry, are expressed in the unit " $\mu\text{m}/\text{second}$ ". The Table shows the results obtained and compares them in the first two cases with results quoted in Example 2 of WO 95/35355 measured by the method of JP 53-2357.

	<u>Noise Units</u> JP 95/35355 (counts/120 sec)	<u>Noise Units</u> SKF Bequiet Test Rig ($\mu\text{m}/\text{sec}$)
(1) Sample 4 of WO 95/35355	7,808	30.5
(2) Sample 12 of WO 95/35355	83	7.2
(3) Commercial polyurea grease	--	3.7
(4) Grease I of invention	--	3.0
(5) Grease II of invention	--	2.7
(6) Grease III of invention	--	2.6

The greases of the invention give rise to appreciably lower noise levels than (2) and (3) (based on the same test rig), being at least 20% better than even the polyurea grease (3). Grease composition (1) omits the dispersant present in grease (2).

In general, the invention achieves superior reduction in noise levels through controlled crystallization during saponification rather than by added chemical components. The prior art greases essentially require dispersant type compounds to be added to achieve noise reduction, *vide* WO 95/35355, EP 0 084 910 and EP 0 718 394.

The Claims Defining the Invention are as Follows:

1. A method of preparing a lubricating grease composition having a major proportion of lubricating base oil and a minor proportion of a simple soap or a complex soap thickener system, or of an organic thickener system or inorganic clay thickener system; which method includes the steps of:
 - (a) agitating and heating the soap-forming or other grease-thickening constituent(s) with at least a portion of the lubricating base oil in a closed reaction vessel over a temperature range and for a period of time sufficient to form a soap or other thickener system,
 - (b) cycling at least a portion of the contents of the reaction vessel, during at least the initial stage of the soap-forming, or other thickening, period, one or more times round a pressure-ventable closed processing loop, including (i) the said agitating and heating in the reaction vessel and (ii) shearing the forming soap or other thickener system in mechanical shearing means.
2. A method as claimed in claim 1, wherein the cycling step (b) is conducted more than once during said initial stage.
3. A method as claimed in claim 1 or claim 2, wherein substantially all of the contents are cycled.
4. A method as claimed in any one of the preceding claims, wherein step (b) is conducted over substantially the full soap-forming, or other thickening, period.
5. A method as claimed in any one of the preceding claims, wherein the shearing is conducted at a clearance of between 50 μm and 2000 μm .
6. The method of claim 5, wherein the shearing is conducted at a clearance of between 100 μm and 500 μm .
7. A method as claimed in any one of the preceding claims, conducted in the absence of any added dispersing agent.

8. A method as claimed in any one of the preceding claims in which the thickener is a simple soap or complex soap thickener system.
9. A lubricating grease composition made in accordance with the method according to any one of the preceding claims.
10. A lithium complex grease composition made by a process according to any one of claims 1 to 8.
11. A grease composition as claimed in claim 9 or claim 10, wherein the lithium complex thickener includes a lithium C₁₂ to C₂₄ hydroxy carboxylate, a lithium salt of a C₃ to C₁₄ hydroxy carboxylic acid or lower alkyl ester thereof.
12. A grease composition as claimed in claim 11, including lithium borate.
13. A grease composition as claimed in any one of claims 9 to 12, wherein the lithium complex thickener includes lithium 12-hydroxy stearate, lithium azelate or salicylate or their methyl esters, and lithium borate.
14. A grease composition as claimed in any one of claims 9 to 13, in which conventional additives, if present, exclude a dispersant.
15. A grease composition as claimed in any one of claims 9 to 14, having a dropping point (ASTM D 566-87) of at least 270°C.
16. A grease composition as claimed in any one of claims 9 to 15, including (i) a major amount by weight of a lubricating base oil; (ii) from 2 to 30 wt.% of a lithium complex soap thickener; and (iii) 0 to 10 wt.% of conventional additives characterized by having a small, uniform internal soap crystal particle size structure and a noise level below 3.5 µm when measured by Anderometry employing a SKF "BEQUIET" test rig MVH 90B.

17. A grease composition as claimed in claim 16, including from 0 to 5 wt.% of conventional additives.