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(54) LUBRICATING GREASE COMPOSITIONS

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(57) ABSTRACT

Lubricating grease composition comprising: (i) a polyalkylene glycol base oil; (ii) a lithium complex thickener; and (iii) a carboxylic acid comprising 18 carbon atoms or greater. The lubricating grease compositions according to the present invention are particularly useful for reducing friction in a dual mass flywheel application.

LUBRICATING GREASE COMPOSITIONS

FIELD OF THE INVENTION

[0001] The present invention relates to lubricating grease compositions, particularly to lubricating grease compositions for use in flywheel applications, in particular, for use in dual mass flywheel applications.

BACKGROUND OF THE INVENTION

[0002] The primary purpose of lubrication is separation of solid surfaces moving relative to one another, to minimise friction and wear. The materials most frequently used for this purpose are oils and greases. The choice of lubricant is mostly determined by the particular application.

[0003] Lubricating greases are the lubricants of choice in a dual mass flywheel application. A dual mass flywheel eliminates excessive transmission gear rattle, reduces gear change/shift effort, and increases fuel economy. Dual mass flywheels are typically fitted to light-duty diesel trucks with standard manual transmissions and to higher performance luxury vehicles to dampen vibration in the drive train. This allows vehicles to be operated for longer periods without long term damage.

[0004] Greases based on lithium soap complexes are known for use in flywheel applications. Such greases have been found to provide satisfactory lubricating properties. However, due to ever increasing demands for higher performance, it would be desirable to provide greases for use in mass flywheel applications which exhibit improved lubrication properties, and in particular, improved friction reducing properties.

SUMMARY OF THE INVENTION

[0005] According to the present invention there is provided a lubricating grease composition comprising:

[0006] (i) a polyalkylene glycol base oil;

[0007] (ii) a lithium complex thickener; and

[0008] (iii) a carboxylic acid comprising 18 carbon atoms or greater.

[0009] According to the present invention there is further provided the use of a lubricating grease composition as described hereinbelow in a dual mass flywheel application.

[0010] According to the present invention there is further provided the use of a lubricating composition as described hereinbelow for reducing friction.

[0011] It has surprisingly been found that the grease compositions of the present invention exhibit excellent friction reducing properties, as well as good stability, good wear properties, high resistance to centrifugal forces and increased grease lifetime.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The lubricating grease of the present invention comprises, as an essential component, a polyalkylene glycol base oil.

[0013] There are no particular limitations regarding the polyalkylene glycol base oil used in lubricating compositions according to the present invention, and various conventional polyalkylene glycols may be conveniently used.

[0014] The polyalkylene glycols (PAG) used according to the invention may exhibit alkylene oxide units with 1 to 6 carbon atoms (—R—O—) as monomer units.

[0015] The polyalkylene glycols may exhibit hydrogen end groups, alkyl, aryl, alkylaryl, aryloxy, alkoxy, alkylaryloxy and/or hydroxy end groups. Alkylaryloxy groups should also be understood to mean arylalkyl (ene)oxy groups and alkylaryl groups to mean arylalkyl(ene) groups (e.g. aryl CH_2CH_2—). The end groups of the alkyl type, including the alkoxy type, or of the aryl types, including the alkylaryl type, aryloxy type and alkylaryloxy type preferably exhibit 6 to 24 carbon atoms, particularly preferably 6 to 18 carbon atoms, based on the aryl types, and preferably 1 to 12 carbon atoms, based on the alkyl types.

[0016] It is preferred that the polyalkylene glycols used herein have a density which is similar to that of the lithium complex soaps (e.g. lithium sebacate, lithium azelate) used in the compositions. Preferably, the polyalkylene glycols used herein have a density of from 900 to 1400 Kg/m^3, more preferably from 950 to 1100 Kg/m^3, even more preferably from 1000 to 1100 Kg/m^3.

[0017] The polyalkylene glycols according to the invention may be either homopolymers, namely polypropylene glycol (and/or polypropylene oxide) or copolymers, terpolymers etc. For the latter cases, the monomer units may exhibit a random distribution or a block structure. If the polyalkylene glycols are not homopolymers, preferably at least 20%, preferably at least 40% of all monomer units are producible from polypropylene oxide (PO), and also preferably, at least 20% of all monomer units of these polyalkylene glycols are producible by using ethylene oxide (EO) (PO/EO copolymers). According to a further embodiment, preferably at least 20%, preferably at least 40% of all monomer units are obtainable from butylene oxide (BO) and, moreover, preferably at least 20% of all monomer units of these polyalkylene glycols are obtainable by using ethylene oxide (BO/EO copolymers).

[0018] In preferred embodiments herein, preferably at least 50%, more preferably at least 80% of all monomer units are producible from propylene oxide, with the remainder producible from ethylene oxide.

[0019] In a particularly preferred embodiment herein, the polyalkylene glycols are homopolymers of propylene oxide. Suitable examples of polypropylene homopolymers are commercially available from Dow Chemicals under the tradename Synalox®, for example, Synalox® 100-150B.

[0020] When (poly)alcohols are used, the starting compound is incorporated into the polymer and, according to the meaning of the invention, also referred to as end group of the polymer chain. Suitable starting groups consist of compounds comprising active hydrogen such as e.g. water, n-butanol, propylene glycol, ethylene glycol, neopentyl glycols such as pentaerythritol, ethylene diamine, phenol, cresol or other (C_1 to C_{16} (mono, di or tri)alkyl) aromatics, (hydroxyalkyl) aromatics, hydroquinone, aminoethanolamines, triethylenetetramines, polyamines, sorbitol or other sugars. Other C—H acidic compounds such as carboxylic acids or carboxylic anhydrides, can also be used as starting compounds. Other suitable starting compounds include longer chain alcohols, such as C_{10} to C_{18} alcohols.

[0021] Preferably, the polyalkylene glycols comprise aryl groups or corresponding heteroaromatic groups, e.g. inserted into the polymer chain, as side groups or end groups; the groups may, if necessary, be substituted with linear or branched alkyl groups or alkylene groups, the alkyl groups or alkylene groups overall exhibiting preferably 1 to 18 carbon atoms.

[0022] Cyclic ether alcohols such as hydroxyfurfuryl or hydroxytetrahydrofuran, nitrogen heterocyclics or sulphur heterocyclics can also be used as starting groups. Such polyalkylene glycols are disclosed in WO 01/57164, the teaching of which is herewith incorporated by reference.

[0023] Preferably, the polyalkylene glycols according to the invention have an average molecular weight (number average) of from 200 to 6000 g/mole, more preferably from 400 to 4000 g/mole, even more preferably from 1000 to 3000 g/mole and especially from 2000 to 3000 g/mole.

[0024] The polyalkylene glycols used according to the invention can be produced by reacting alcohols, including polyalcohols, as starting compounds with oxiranes such as ethylene oxide, propylene oxide and/or butylene oxide. Following the reaction, these possess only one free hydroxy group as end group. Polyalkylene glycols with only one hydroxy group are preferred over those with two free hydroxy groups. Polyalkylene glycols which, e.g. after a further etherification step, comprise no free hydroxy groups any longer are particularly preferred regarding the stability, hygroscopicity and compatibility. The alkylation of terminal hydroxyl groups leads to an increase in the thermal stability. Thus, in an especially preferred embodiment according to the present invention, the PAG base oil comprises end-capped PAG, i.e. where no free hydroxyl groups are present.

[0025] Preferably, the lubricating composition comprises at least 30 wt. % PAG base oil, preferably at least 50 wt. %, more preferably at least 70 wt. %, based on the total weight of the lubricating composition. It is even more preferred that as the base oil only (one or more) PAG base oil(s) is used.

[0026] According to a preferred embodiment of the present invention, the PAG base oil has a kinematic viscosity at 40° C. (according to ASTM D445) of from 32 to 690, preferably from 100 to 300, more preferably from 150 to 250 mm^2/s.

[0027] In addition to the polyalkylene glycol base oil, it is possible to include further base oils, which may be any of the conventionally used lubricating oils of mineral or synthetic origin. However, in a preferred embodiment of the invention the base oil consists only of one or more polyalkylene glycol base oils.

[0028] Base oils of mineral origin may be mineral oils, for example produced by solvent refining or hydro-processing. Base oils of synthetic origin may typically be mixtures of C_{10-50} hydrocarbon polymers, for example liquid polymers of alpha-olefins. They may also be conventional esters, for example polyol esters. The base oil may also be a mixture of these oils. Preferably the base oil is that of mineral origin sold by the Royal Dutch/Shell Group of Companies under the designations “HVI” or “MVIN”, is a polyalphaolefin, or a mixture of the two. Synthetic hydrocarbon base oils, for example those sold by the Royal Dutch/Shell Group of Companies under the designation “XHVI” (trade mark) may also be used. When present, 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.

[0029] In addition to the polyalkylene glycol base oil, the lubricating grease compositions of the present invention further comprise a lithium soap complex thickener.

[0030] The amount of lithium soap complex present in the grease is preferably from 2% to 30%, preferably from 5% to 20%, by weight of the composition.

[0031] In preferred embodiments, the lithium soap complex comprises a lithium soap of a C_{12} to C_{24} hydroxy fatty acid and a lithium soap of a C_2 to C_{12} aliphatic dicarboxylic acid.

[0032] More preferably the lithium soap of the hydroxy fatty acid is a C_{16} to C_{20} hydroxy fatty acid. A particularly preferred hydroxy fatty acid is hydroxystearic acid, for example, 9-hydroxy, 10-hydroxy, or 12-hydroxystearic acid, more preferably the latter. Ricinoleic acid which is an unsaturated form of 12-hydroxystearic acid having a double bond in the 9-10 position, can also be used. Other suitable hydroxy fatty acids include 12-hydroxybehenic acid and 10-hydroxypalmitic acid.

[0033] The dicarboxylic acid is preferably a C_4 to C_{12}, more preferably C_6 to C_{10}, aliphatic dicarboxylic acid. Examples of suitable acids include oxalic, malonic, succinic, glutaric, adipic, suberic, pimelic, azelaic, dodecanedioic and sebacic acids. Azelaic and sebacic acids are especially preferred.

[0034] The C_{12} to C_{24} hydroxy fatty acid and the C_2 to C_{12} aliphatic dicarboxylic acid are preferably present in a weight ratio of from 20:1 to 1:1, preferably from 10:1 to 1:1, more preferably from 8:1 to 3:1.

[0035] Another essential component of the lubricating grease compositions of the present invention is a long chain carboxylic acid having at least 18 carbon atoms. Preferably, the long chain carboxylic acid having at least 18 carbon atoms is present in an amount of from 0.1% to 10%, preferably from about 1% to about 10%, more preferably from about 1% to about 5%, by weight of the composition.

[0036] Preferably the long chain carboxylic acid is selected from carboxylic acids having from 18 to 90 carbon atoms. In particularly preferred embodiments, the long chain carboxylic acid is selected from dimer and trimer acids, which are polycarboxylic acids having the general formula $R(COOH)_n$, wherein n is 2 or 3, and where R is a hydrocarbon radical within the range of 24 to 90 carbon atoms, preferably 36 to 54 carbon atoms, which may be saturated or unsaturated. Linoleic dimer acid is formed by reaction of two molecules of linoleic acid in a typical Diels-Alder reaction. Linoleic trimer acid is a C_{54} tricarboxylic acid formed by polymerization of three molecules of linoleic acid which are linked together by their unsaturation. Dimers and trimers of linoleic acid are commercially available from Oleon Chemicals under the tradename Radiacid and from Arizona Chemicals under the tradename Unidyme. Particularly preferred examples of dimers and trimers of linoleic acid are Radiacid 0975 and Radiacid 0980 commercially available from Oleon Chemicals, Belgium, and Unidyme 12 (C_{18} dimer) commercially available from Arizona Chemical, USA.

[0037] Various conventional grease additives may be incorporated into the lubricating greases of the present invention, in amounts normally used in this field of application, to impart certain desirable characteristics to the grease, such as oxidation stability, tackiness, extreme pressure properties and corrosion inhibition. Suitable additives include one or more extreme pressure/antiwear agents, for example zinc salts such as zinc dialkyl or diaryl dithiophosphates, borates, substituted thiadiazoles, polymeric nitrogen/phosphorus compounds made, for example, by reacting a dialkoxy amine with a substituted organic phosphate, amine phosphates, sulphurised sperm oils of natural or synthetic origin, sulphurised lard, sulphurised esters, sulphurised fatty acid esters, and similar sulphurised materials, organo-phosphates for example according to the formula $(OR)_3P{=}O$ where R is an alkyl, aryl or aralkyl group, and triphenyl phosphorothionate; one or more overbased metal-containing detergents, such as calcium or magnesium alkyl salicylates or alkylarylsulphonates; one or more ashless dispersant additives, such as reaction products of polyisobutenyl succinic anhydride and an amine or ester; one or more antioxidants, such as hindered phenols or amines, for example phenyl alpha naphthylamine; one or more antirust additives; one or more friction-modifying additives; one or more viscosity-index improving agents; one or more pour point depressing additives; and one or more tackiness agents. Solid materials such as graphite, finely divided molybdenum disulphide, talc, metal powders, and various polymers such as polyethylene wax may also be added to impart special properties.

[0038] To reduce friction levels, those skilled in the art have largely looked to using organic molybdenum-based formulations, and there are numerous proposals in patent literature of such lubricating compositions.

[0039] The present invention will now be described by reference to the following Examples:

Examples 1 to 3 and Comparative Example A

[0040] The lubricating greases of Examples 1 to 3 and Comparative Example A were prepared by the following procedure.

[0041] 50% of the base oil is charged in an autoclave together with 12-hydroxystearic acid, sebacic acid and lithium hydroxide monohydrate and 100 ml of water. The autoclave is closed and heated up to 145° C. After reaching the venting temperature the venting valve is opened and steam is released for 30 minutes. When the steam pressure is 0 bar, with the venting valve still open, heating is started up to a temperature of 215° C. After reaching a temperature of 215° C., the autoclave is cooled down with jacket cooling of 1° C./ruin to reach 165° C. After reaching 165° C. the remaining 50% of base oil is charged in the vessel. Then the product is cooled to 80° C. and any additives are charged in the vessel. Then the product is homogenized with a triple roll mill.

[0042] The compositions of the prepared greases are set out in Table 1 below. Example 1 contains 4% of a specified dimer of an unsaturated C18 fatty acid. Example 2 contains 4% of a specified trimer of an unsaturated C18 fatty acid. Example 3 contains a C18 saturated fatty acid. Comparative Example A contains no dimers or trimers of C18 fatty acids.

TABLE 1

	Comparative Example A	Ex. 1	Ex. 2	Ex. 3
Synalox 100-150B[1]	83.82	79.82	79.82	79.82
LiOH—$\mathrm{H}_2$0	2.3	2.3	2.3	2.3
Sebacic acid	1.88	1.88	1.88	1.88
12-hydroxystearic acid	10	10	10	10
Radiacid 0975[2]	0	4	0	0
Radiacid 0980[3]	0	0	4	0
Radiacid 0152[4]	0	0	0	4
Naugalube AMS[5]	0.5	0.5	0.5	0.5
Ralox LC[6]	0.5	0.5	0.5	0.5
Irganox L57[7]	0.5	0.5	0.5	0.5
Valirex Zn 8.0[8]	0.5	0.5	0.5	0.5

[1] polypropylene glycol homopolymer commercially available from Dow Chemicals
[2] dimer of C_{18} fatty acid commercially available from Oleon Chemicals
[3] trimer of C_{18} fatty acid commercially available from Oleon Chemicals
[4] C_{18} saturated fatty acid commercially available from Oleon Chemicals
[5] commercially available from Chemtura, USA
[6] commercially available from Raschig, Ludwigshafen, Germany
[7] commercially available from CIBA Geigy Specialties, Switzerland
[8] commercially available from Corm Van Loocke, Belgium

Example 4

Measurement of Friction Coefficient

[0043] The friction coefficients of Examples 1 to 3 and Comparative Example A were measured using the test method described below.

[0044] The friction testing of a mass fly wheel can be done with a dynamic torsion test rig. It is necessary to use completely new components for all inner parts of the mass fly wheel which have to be in line with material specification. The mass fly wheel is conditioned first in the torsion test rig at various speeds and angles for at least 4 hours to get constant surface condition. The mass fly wheel is filled with the grease (of the Examples or Comparative Example) according to the filling guideline of the testing part and then is tested at 120° C. temperature, 2000 rpm and +/−30° angle oscillation with 0.25 Hz. The friction value of the mass fly wheel corresponds to the torque needed for one complete oscillation cycle. The friction coefficient is calculated according to the maximum torque after displacement from each direction at the zero crossing minus the minimum torque redisplacement of each direction at the zero crossing divided by 2.

[0045] The friction coefficients of Examples 1 to 3 and Comparative Example A are set out in Table 2 below.

TABLE 2

Example	Friction Coefficient
A*	0.106
1	0.059
2	0.059
3	0.082

*Comparative Example

[0046] It can be seen from the results in Table 2 that the addition of the dimer (C_{36}) or trimer (C_{54}) acids to the PAG plus lithium soap complex results in a substantial reduction in friction coefficient.

1. A lubricating grease composition comprising:
(i) a polyalkylene glycol base oil;
(ii) a lithium complex thickener; and
(iii) a carboxylic acid comprising 18 carbon atoms or greater.

2. The lubricating grease composition according to claim **1** wherein the carboxylic acid comprises from 18 to 54 carbon atoms.

3. The lubricating grease composition according to claim **1** wherein the carboxylic acid is selected from dimer and trimer acids having the general formula $R(COOH)_n$, wherein n is 2 or 3, and wherein R is a hydrocarbon radical having from 36 to 54 carbon atoms.

4. The lubricating grease composition according to claim **3** selected from dimers and trimers of linoleic acid.

5. The lubricating composition according to any of claim **4** wherein the lithium complex thickener comprises a lithium soap of a C_{12} to C_{24} hydroxycarboxylic acid and a lithium soap of a C_2 to C_{12} dicarboxylic acid.

6. The lubricating composition according to claim **5** wherein the lithium soap of a C_{12} to C_{24} hydroxycarboxylic acid is lithium 12-hydroxy stearate.

7. The lubricating composition according to claim **6** wherein the C_2 to C_{12} dicarboxylic acid is selected from azelaic acid, sebacic acid and mixtures thereof.

8. The lubricating composition according to claim **7** wherein said polyalkylene glycol base oil is a homopolymer of polypropylene glycol.

9. The lubricating grease composition according to claim **8** wherein said polyalkylene glycol base oil has a density of from 900 to 1400 Kg/m^3.

10. (canceled)

11. (canceled)

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