



(11)

EP 3 212 747 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:

12.08.2020 Bulletin 2020/33

(21) Application number: **15791267.6**

(22) Date of filing: **30.10.2015**

(51) Int Cl.:

C10M 169/00 (2006.01)

(86) International application number:

PCT/EP2015/075237

(87) International publication number:

WO 2016/066792 (06.05.2016 Gazette 2016/18)

(54) **GREASE COMPOSITIONS**

SCHMIERFETTZUSAMMENSETZUNGEN

COMPOSITIONS DE GRAISSE

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **31.10.2014 GB 201419437**

(43) Date of publication of application:

06.09.2017 Bulletin 2017/36

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to grease compositions, methods for manufacturing the grease compositions, and the use of the grease compositions for lubricating bearings, gears and couplings.

BACKGROUND OF THE INVENTION

10 **[0002]** Grease compositions are widely used for lubricating bearings and other structural components. A grease is an essential product to reduce, for example, wear, friction, running temperatures and energy losses. Greases are materials which comprise a base oil that is thickened with a metal soap, and they are usually prepared by reacting a metal hydroxide with a fatty acid in the presence of the base oil. Conventional metal soap greases require an energy intensive grease cooking and milling process in order to achieve proper thermo-mechanical stability. Conventional metal soap greases
15 can still be sensitive to poor thermo-mechanical stability and can require additional treatments. It is known to improve further the stability, and thus the lubricating capacity, of conventional greases by adding solid additives during the thickening process. Examples of such solid additives are, for example, molybdenum disulfide, graphite, zinc oxide and/or a silica gel. The process of grease cooking and milling and additional treatments is relatively expensive because it is carried out at an elevated temperature and over a relatively long period of time. Moreover, the greases so prepared are still unsuitable for a variety of applications, and not all conventional greases are suitable for food and beverage processing applications.

[0003] In WO 2011/015337 A2, a non-hydroxide grease composition is described comprising a base oil and a thickener which comprises amorphous hydrophilic silicon oxide particles and one or more metal salts of different organic acids. US 8,455,415 discloses a grease composition including a base oil, a metal soap thickener formed from for instance
25 lithium and fatty acid ester, and nanoparticles formed from SiC or diamond and having an average primary particle size of 5 nm or smaller.

[0004] Consequently, there is a need for greases which can easily be manufactured at low costs, which are stable and show highly attractive lubricating properties in terms of low friction performance. In addition, there is a need for greases that are biodegradable, environmentally benign and food compatible.

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SUMMARY OF THE INVENTION

[0005] Object of the present invention is to provide grease compositions which show excellent lubricating properties such as grease life performance, corrosion wear and thermo and mechanical stability, and which can easily be manufactured at low costs and/or are more environmental friendly.

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[0006] Surprisingly, it has now been found that this can be established when use is made of a base oil and a thickener which comprises amorphous hydrophilic fumed silicon oxide particles and a particular ester.

[0007] Accordingly, the present invention relates to a grease composition as defined in claim 1.

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[0008] The present invention in addition relates to a grease composition comprising a base oil and a thickener which comprises amorphous hydrophilic fumed silicon oxide particles and one or more esters that contain one or more unsaturated C-C bonds and at least one OH group, wherein the amorphous hydrophilic fumed silicon oxide particles have a BET specific surface area of at least 10 m²/g and at least 80% of the amorphous hydrophilic fumed silicon oxide particles have a particle size in the range of from 5 nm to 50 nm, and wherein the amount of the thickener is in the range of from 0.1-40% by weight, based on the total weight of the grease composition.

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[0009] Suitably, the thickener comprises in addition one or more metal salts such as metal sulphonates, metal sulphates, metal phosphates and/or metal phosphonates.

[0010] The grease compositions according to the present invention show an attractive low friction performance, whereas at the same time they can easily be manufactured at low costs and/or are more environmental friendly.

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DETAILED DESCRIPTION OF THE INVENTION

[0011] The thickener to be used in the present grease composition comprises one or more esters that contain at least one OH group. Preferably, the one or more esters contain one or more unsaturated C-C bonds and at least one OH group.

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[0012] Esters are derived from an acid in which one OH group has been replaced by an alkoxy group (-O-). Often esters are derived from a carboxylic acid and an alcohol. Esterification is the chemical reaction of the acid and the alcohol to form the ester and is usually in the presence of a catalyst, a dehydrating agent.

[0013] Suitably, the one or more esters are diesters. Suitably, the one or more esters contain two or more unsaturated C-C bonds. Suitably, the one or more esters contain at least two OH groups. Suitably, the one or more esters contain

at least two unsaturated C-C bonds and at least one OH group. Preferably, the one or more esters contain at least two unsaturated C-C bonds and at least two OH groups. Suitably, the one or more esters are metal salts. Suitably, the one or more esters comprise glycerol esters, such as for example triglycerol esters.

[0014] Suitably, the one or more esters are esterified fatty acids that contain at least one OH group. It will be understood that fatty acids are aliphatic monocarboxylic acids derived from, or contained in esterified form in an animal or vegetable fat, oil or wax. In accordance with the present invention use can be made of natural and synthetic fatty acids. Suitable fatty acids from which the esterified fatty acids can be made include caprylic acid, pelargonic acid, capric acid, lauric acid, linderic acid, rayristic acid, tsuzuic acid, physetoleic acid, myristoleic acid, pentadecylic acid, palmitic acid, palmitoleic acid, margaric acid, stearic acid, 12-hydroxystearic acid, petroselinic acid, oleic acid, elaidic acid, vaccenic acid, linolic acid, linolenic acid, elaeostearic acid, tuberculostearic acid, arachidic acid, eicosadienic acid, eicosatrienic acid, arachidonic acid, behenic acid, lignoceric acid, nervonic acid, hexadocosanic acid, octadocosanic acid and erucic acid.

[0015] Suitably, use can be made of a mixture of different esterified fatty acids. Suitable examples of such esterified fatty acids are for example alkyl oleate esters and alkyl linoleate esters such as methyl oleate ester, ethyl oleate ester and ethyl linoleate ester. The grease compositions may also contain a double esterified fatty ester in which two ester groups are present. Suitable examples of such diesters are for instance dioctylsebacic ester, dioctylsebacate ester and diisooctyl sebacate ester. Suitably, the one or more (di)esters contain two or more unsaturated C-C bonds. In addition, the (di)esters contain at least one OH group. Suitable examples of such esters include such methyl-12-hydroxystearate ester, 9-Octadecenoic acid, 12 hydroxy methyl ester and hydroxy palmitic ester.

[0016] The one or more esters to be used in accordance with the present invention have a relative polarity which is introduced by means of an OH-group on for example a secondary position in the fatty acid chain. In this way an improved low friction performance could be realized.

[0017] The esters to be used in accordance with the present invention include branched and unbranched esters. The esters may contain an amine group and/or amide group.

[0018] Suitably, the thickener comprises in addition one or more metal salts such as metal sulphonates, metal sulphates, metal phosphates and/or metal phosphonates. When the one or more esters are metal salts, the amount of metal (salt(s)) is in the range of from 0.1-40% by weight, based on the total weight of the grease composition. When one or more esterified fatty acids are metal salts, the amount of metal salt(s) is in the range of from 0.1-40% by weight, based on the total weight of the grease composition. The metal in the metal salts is preferably an alkali metal or an alkaline earth metal of Groups 1 and 2 of the Periodic System of Elements, and bismuth. Suitable examples of metals include lithium, potassium, sodium, calcium, aluminium, rubidium, cesium, francium, beryllium, strontium, barium, radium, bismuth and magnesium. In addition it is noted that the metal in the metal salt to be used can be a semi-metal such as borium. According to a preferred embodiment according to the present invention, the metal is an alkaline earth metal, most preferably calcium.

[0019] Suitably, the thickener comprises in addition one or more metal salts such as metal sulphonates, metal sulphates, metal phosphates and/or metal phosphonates.

[0020] The grease compositions according to the present invention are non-hydroxide grease compositions. Non-hydroxide grease compositions in accordance with the present invention do not contain impurities such as excess amounts of hydroxide which are normally present in greases that are prepared in conventional lime soap manufacturing processes. The non-hydroxide grease compositions according to the present invention are suitably substantially free of free hydroxide ions and/or metal hydroxide. Preferably, the present non-hydroxide grease compositions contain less than 0.2% by weight, and more preferably less than 0.1% by weight of free hydroxide ions and/or metal hydroxide, based on the total weight of the grease composition. Preferably, the present non-hydroxide grease compositions are substantially free of free hydroxide ions and/or metal hydroxide. Preferably, the present grease compositions contain less than 0.2% by weight, and more preferably less than 0.1% by weight of metal hydroxide, based on the total weight of the grease composition. Most preferably, the present non-hydroxide grease compositions are completely free of metal hydroxide. It will be understood that OH-groups present on the amorphous hydrophilic fumed silicon oxide particles or in a fatty acid such as 12-hydroxy stearate or the metal salt of such a fatty acid are not to be considered free hydroxide ions since they are bonded to silicon atoms or to a carbon atom of the fatty acid. The thickener to be used in accordance with the present invention is suitably a non-saponified thickener.

[0021] Examples of esters containing unsaturated C-C bonds include 1,2-dilinoeoyl-3-oleoyl-racglycerol, glyceryl-trilinoeate, glyceryl monostearate, palmitoleic acid ethyl ester, glyceryl trioleate, ethyl oleate, methyl oleate, methyl linoleate, methyl linolenate, oleyl oleate, propyl oleate, myristyl oleate, ethyl palmitoleate, ethyl linoleate, oleyl stearate, oleyl myristate, oleyl erucate, methyl erucate, ethyl erucate and linolein.

[0022] Examples of esters containing an OH group include glyceryl-1,2-dioloate-3-palmitate, glyceryl behenate, glyceryl adipate, glyceryl myristate, glyceryl stearate citrate, glyceryl caprylate, glyceryl laurate, glyceryl arachidate, glyceryl palmitate, glyceryl hydroxystearate, glyceryl stearate, Methyl 12-hydroxyoctadecanoate and hydroxyl palmitic ester.

[0023] Examples of esters containing an OH group and an unsaturated C-C bond include glyceryl ricinoleate ester, glyceryl linoleate, glyceryl linolenate, glyceryl palmitoleate, glycerol dioleate, glyceryl erucate, glyceryl oleate, trieth-

anolamine oleate, ethyl ricinoleate, methyl ricinoleate, O-acetylricinoleic acid methyl ester and ricinolein.

[0024] Examples of diesters include diisooctylsebacic acid ester, dioctyladipate acid ester, dioctylsebacate ester, dimethylsebacate ester and diethylsebacate ester.

[0025] The present grease composition may also comprise one or more amides.

Suitably, the amides to be used in accordance with the present invention contain one or more unsaturated C-C bonds and/or at least one OH group. Suitably, the amides to be used in accordance with the present invention contain one or more unsaturated C-C bonds and at least one OH group. Suitably, the amides contain two or more unsaturated C-C bonds. Suitably, the amides contain two or more unsaturated C-C bonds and at least one OH group, preferably at least two OH groups.

Suitable amides that contain one or more unsaturated C-C bonds include unsaturated amides such as oleamide and linoleamide; diamides such as ethylene bis stearamide, hydroxy ethyl ethylene bis oleamide, ethylene bis-12-hydroxystearamide and bishydroxyethyl oleylamine; and OH-group containing amides such as hydroxy ethyl ethylene bis oleamide, ethylene bis-12-hydroxystearamide.

Preferably, the unsaturated amides are unsaturated fatty acid amides, more preferably the amides are metal salts of unsaturated fatty acid amides. The amides to be used in accordance with the present invention include branched and unbranched amides. The amides may contain an ester group.

The present invention preferably provides a grease composition comprising a base oil and a thickener which comprises amorphous hydrophilic fumed silicon oxide particles, one or more metal sulphonates, metal sulphates, metal phosphates and/or metal phosphonates, a calcium salt of 12-hydroxy stearic acid and one or more esters that contain at least one OH group, wherein the amorphous hydrophilic fumed silicon oxide particles have a BET specific surface area of at least 10 m²/g and at least 80% of the amorphous hydrophilic fumed silicon oxide particles have a mean particle size of 5 nm to 50 nm, and wherein the amount of the thickener is 0.1-40% by weight, based on the total weight of the grease.

The nature of the base oil to be used in accordance with the present invention is not essential. The base oil may be selected from the group consisting of mineral base oils and synthetic base oils. Mineral base oils are derived from crude oils and are either formulated on the basis of aromatic, paraffinic and/or naphthenic base oils. Further, a wide range of synthetic base oils is known and they include esters, poly-alpha-olefins, polysiloxanes and the like.

The base oil to be used in accordance with the present invention may comprise a base oil blend. Suitably, blends of mineral base oils and synthetic base oils may be used. The base oil in this invention is one which may ordinarily be used as the base oil of a lubricating oil or as the base oil of a grease, and there are no special restrictions. As examples mention may be made of mineral oils, synthetic oils, animal and plant oils, and mixtures thereof. In particular it is possible to use, singly or as mixtures, base oils which belong to Group I, Group II, Group III, Group IV and so on of the API (American Petroleum Institute) base oil categories. Group I base oils include, for example, paraffinic mineral oils obtained by a suitable combination of refining processes such as solvent refining, hydrotreating, and dewaxing in respect of lubricating oil - o fractions obtained by atmospheric distillation of crude oil. Group II base oils include, for example, paraffinic mineral oils obtained by a suitable combination of refining processes such as hydrotreating and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil. Group II base oils refined by hydrotreating methods such as the Gulf Company method have a total sulphur content of less than 10 ppm and an aromatic content of not more than 5% and so are suitable for this invention. Group III base oils and Group 11+ base oils include paraffinic mineral oils manufactured by a high degree of hydrotreating in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil, base oils refined by the Isodewax process which dewaxes and substitutes the wax produced by the dewaxing process with isoparaffins, and base oils refined by the Mobil wax isomerisation process. These too are suitable for use in this invention. Concrete examples of synthetic oils include polyolefins, polyoxyalkylene glycols such as polyethylene glycol or polypropylene glycol, esters such as di-2-ethylhexyl sebacate or di-2-ethylhexyl adipate, polyol esters such as trimethylolpropane esters or pentaerythritol esters, perfluoroalkyl ethers, silicone oils, polyphenyl ethers, and so on.

The aforementioned polyolefins include polymers of various olefins or hydrides thereof. Any olefin may be used, and as examples mention may be made of ethylene, propylene, butene and [alpha]-olefins with five or more carbons. In the manufacture of polyolefins, one of the aforementioned olefins may be used singly or two or more may be used in combination. Particularly suitable are the polyolefins called poly-[alpha]-olefins (PAO). These are base oils of Group IV. GTL (gas to liquid) base oils synthesised by the Fischer-Tropsch method of converting natural gas to liquid fuel have a very low sulphur content and aromatic content compared with mineral oil base oils refined from crude oil and have a very high paraffin constituent ratio, and so have excellent oxidative stability, and because they also have extremely small evaporation losses, they are suitable as base oils for this invention. As typical examples of animal and plant oils mention may be made of castor oil and rape-seed oil. The various aforementioned oils may be used singly or in mixtures for the base oil. The aforementioned examples are listed singly but the invention is not limited thereby.

Preferably, the base oil or the base oil blend to be used in accordance with the present invention has a kinematic viscosity in the range of 1 to 60 000 cSt at a temperature of 40 °C according to DIN 51562/1. Suitable base oils include

ISO VG 68, ISO VG 46, ISO VG 32, ISO VG 22, ISO VG 15 and ISO VG 10 oils.

[0033] The silicon oxide particles to be used are derived from an amorphous hydrophilic fumed silicon oxide. Fumed silicon oxide is an exceptionally pure form of silicon oxide made from silica tetrachloride as a starting material, as is well known in the art. Suitable sources for the fumed silicon oxide are Aerosil(R) which is commercially available from Evonik Industries (formerly known as Degussa) or Cap-o-Sil(R) which is commercially available from Cabot Corporation.

[0034] Suitably, the amorphous hydrophilic fumed silicon oxide particles have a BET specific surface area of at least 50 m²/g, more preferably at least 75 m²/g, yet even more preferably at least 100 m²/g, even yet more preferably at least 125 m²/g and most preferably at least 150 m²/g. Although it is preferred that the BET specific surface area is as high as possible, it will usually not be higher than 500 m²/g. Methods for determining the BET specific surface area are well known in the art.

[0035] In some embodiments of the present invention, the hydrophilic metal oxide particles have a BET specific surface area of less than 50 m²/g.

[0036] According to the present invention at least 80% of the amorphous hydrophilic fumed silicon oxide particles have a particle size of 5 nm to 50 nm, preferably of 5-40 nm, more preferably of 10-40 nm and most preferably of 20-40 nm. The total particle size distribution of the amorphous silicon oxide particles is preferably in the range of 1-50 nm.

[0037] The grease compositions according to the invention may additionally comprise other thickening components, e.g. polymers or other fatty compounds that contain one or more OH-groups and/or one or more unsaturated bonds and/or one or more ester groups and/or one or more aromatic groups. Such thickening components can suitably be present in an amount of less than 3% by weight, preferably less than 2% by weight, based on the total weight of the grease composition.

[0038] The grease compositions according to the present invention may comprise other additives to tailor its suitability to a certain use as is well known in the art. Such additives include antiwear agents, anti-corrosion agents, rust inhibitors, friction modifiers, anti-oxidants, VI-improvers and the like as is well known by the person skilled in the art. As suitable examples of such additives sulphonates, sulphates, phosphates and/or phosphonates can be mentioned. Suitable sulphonates include for instance methyl ester sulphonate, sodium methyl ester sulphonate and calcium sulphonate. Suitable sulphates include for example calcium sulphate, sodium dodecyl sulphate and sodium lauryl sulphate. Suitable phosphates include for instance calcium hydrogen phosphate and amine phosphate. Suitable phosphonates include for example calcium phosphonate ester and other phosphonate esters.

[0039] Other suitable additives include silanes, (alkylated) siloxanes, metal hydroxide silicates, silanols, hydrosilicates, metal bonded silicon compound such as Mg₃(Si₂O₅)(OH)₂. Examples of such additives are for instance polydimethyl siloxane oil, hexamethyldisiloxane, magnesium hydrosilicate and other phyllosilicates. As well as polymethylsilsesquioxane, hydrated (metal)silicates, amorphous silica, and synthetic silica gels, which additives are all used to improve polymer performance. Such other additives can suitably be present in an amount in the range of from 1-40% by weight, preferably 2-20% by weight, based on the total weight of the grease composition. In case the grease composition contains a high amount of such other additives, e.g. 20-40% by weight, based on total weight of the grease composition, the grease composition will display paste-type properties. Hence, the grease composition in accordance with the present invention also includes pastes. The other additives may also include small amounts (less than 3% by weight, preferably less than 2% by weight, based on the total weight of the grease composition) of further metal salts of fatty acids, but such metal salts will not substantially contribute to the formation of the grease thickener. In that case the grease composition will contain more than four metal salts of different fatty acids.

[0040] The present grease compositions may in addition also contain a small amount of metal hydroxide. Suitable metal hydroxides include potassium hydroxide, aluminium hydroxide, calcium hydroxide, lithium hydroxide, sodium hydroxide, magnesium hydroxide, barium hydroxide and bismuth hydroxide. Other suitable additives include polypropylene, polyethylene, urea, bentonite, and other greases such as (complex) greases and PTFE/PFPE greases.

[0041] A common disadvantage of conventional manufacturing methods is that it requires a multiple number of hours for blending the various components, gelling and cooling of the grease composition. At a batch scale of about 1-5 metric tons, the total cooking (gelling) and cooling can take about four hours or more, whereas grease milling can require two or more hours. Usually, the total manufacturing time takes about eight hours. However, the grease compositions according to the present invention can be prepared in a very short manufacturing process, wherein blending, gelling and cooling is preferably performed within one hour, more preferably within half an hour period. The mechanical treatment, preferably grease milling, in accordance with the present invention for a 5 metric ton volume can require about two or two and a half hours. In addition, it is observed that conventional grease manufacturing processes are carried out at high temperatures, typically in the range of from 170-220 °C, whereas the present grease composition can suitably be prepared at a temperature below 90 °C, including room temperature.

[0042] The present invention also provides methods for preparing the present grease compositions. In accordance with the present invention the components of the present grease compositions can be mixed in any possible order of sequence. Preferably, the amorphous hydrophilic fumed silicon oxide particles and the one or more esters that contain at least one OH group are subjected to a mechanical treatment, a thermal treatment or to both a mechanical treatment

and a thermal treatment. Hence, (a) the amorphous hydrophilic fumed silicon oxide particles or the one or more esters that contain at least one OH group are subjected to a mechanical treatment and/or thermal treatment; (b) a mixture of the amorphous hydrophilic fumed silicon oxide particles and the one or more esters that contain at least one OH group is subjected to a mechanical treatment and/or thermal treatment; or (c) a mixture of the base oil, the amorphous hydrophilic fumed silicon oxide particles and the one or more esters that contain at least one OH group is subjected to a mechanical treatment and/or thermal treatment. Preferably, the amorphous hydrophilic fumed silicon oxide particles, the one or more esters that contain at least one OH group, or a mixture of these components is before or after mixing with the other component(s) subjected to a mechanical treatment, a thermal treatment or to both a mechanical treatment and a thermal treatment.

[0043] As indicated above, the grease composition may comprise any further additives. Such further additives can be added to one or more of the components at any stage of the preparation process of the grease composition.

[0044] Hence, the present invention also relates to a method for manufacturing a grease composition according to the present invention, which method comprises the following sequential steps:

(a) subjecting the amorphous hydrophilic fumed silicon oxide particles to a mechanical treatment, a thermal treatment or to both a mechanical treatment and a thermal treatment; and

(b) mixing the amorphous hydrophilic fumed silicon oxide particles so obtained with the base oil and one or more esters that contain at least one OH group to form a grease composition.

[0045] In case use is made of a plurality of esters, the esters may optionally be processed together with the amorphous hydrophilic fumed silicon oxide particles in step (a).

[0046] According to another embodiment of the present invention, the amorphous hydrophilic fumed silicon oxide particles are first mixed with the base oil and the one or more esters that contain at least one OH group to form a grease composition, whereafter the grease composition so formed is subjected to the mechanical treatment, the thermal treatment or to both the mechanical treatment and the thermal treatment.

[0047] Accordingly, the present invention also relates to a method for manufacturing a grease according to the present invention, which method comprises the following sequential steps: (a) mixing the amorphous hydrophilic fumed silicon oxide particles with the base oil and one or more esters that contain at least one OH group to form a grease composition; and (b) subjecting the grease composition so formed to a mechanical treatment, a thermal treatment or to both a mechanical treatment and a thermal treatment. The mechanical treatment is preferably a milling step which can be performed in any suitable milling apparatus, e.g. a high pressure homogeniser, a colloid mill, a three-roller mill (e.g. a three-roller mill) or a worm gear mill. Preferably, the milling apparatus is a worm gear milling apparatus. The milling step can be performed under inert conditions, i.e. in the absence of air or oxygen and/or in the absence of water (vapour). The thermal treatment is preferably a heating step. The heating step preferably involves heating at a temperature in the range of 30-120 °C, more preferably 40-110 °C and in particular 45- 90 °C. In this heating step, the water content of the amorphous hydrophilicfumed silicon oxide particles is reduced, preferably to a water content of the amorphous hydrophilic fumed silicon oxide particles of less than 5% by weight, more preferably less than 1% by weight, even more preferably less than 0.5% by weight, yet even more preferably less than 0.25% by weight, based on the total weight of the amorphous hydrophilic fumed silicon oxide particles. The water content of the amorphous hydrophilic fumed silicon oxide particles is usually more than 0.01% by weight, based on the total weight of the amorphous hydrophilic fumed silicon oxide particles.

[0048] Most preferably, the grease composition is manufactured by optionally subjecting the amorphous hydrophilic fumed silicon oxide particles to a thermal treatment, preferably a heating step, to reduce the water content of the amorphous hydrophilic fumed silicon oxide particles, followed by mixing the amorphous hydrophilic fumed silicon oxide particles with the base oil and the one or more esters that contain at least one OH group to form a grease composition, whereafter the grease composition so formed is subjected to a mechanical treatment, preferably a milling step.

[0049] As disclosed above, the grease composition according to the present invention comprises a base oil, amorphous hydrophilic fumed silicon oxide particles, and one or more esters that contain at least one OH group, wherein the amount of the metal salts(s) is 0.1-40% by weight, based on the total weight of the grease composition.

[0050] Suitably, the amount of the amorphous hydrophilic fumed silicon oxide particles will be 0.1-20% by weight, preferably 1-5% by weight, based on the total weight of the amorphous hydrophilic fumed silicon oxide particles and the esters. The skilled person will understand how such amounts can be realised starting from the respective starting materials.

[0051] According to the present invention, the total amount of the esters, is within a range of 0.1-20% by weight, based on the total amount of the grease composition.

[0052] The grease composition according to the present invention can be used in many applications. However, it is in particular useful for lubricating a bearing, preferably a rolling element bearing, e.g. a spherical roller bearing, a taper roller bearing, a cylindrical roller bearing, a needle roller bearing, a ball bearing, and may also be used to lubricate a sliding or plain bearing. It is furthermore very useful in coupling and gearing applications.

[0053] The grease compositions according to the present invention encompass NLGI (National Lubricating Grease Institute) grades ranging from NLGI grade 000 to NLGI grade 6. Preferably, the grease compositions according to the present invention have a dropping point of at least 70 °C up to about 200 °C according to ASTM D-2265.

[0054] When used in low loading gearings, the grease composition has preferably a NLGI grade of 000 to 1. When used in high loading gearings, the grease composition has preferably a NLGI grade of 0 to 2. When used in bearings, the grease composition has preferably a NLGI grade of 1 to 4, more preferably a NLGI grade of 2 or 3 and most preferably a NLGI grade of 2.

Examples

[0055] The performance of four grease compositions has been tested on tribological and friction performance on the Ball-on-disc, the Mini Traction Machine, at Imperial College, London UK. In each case the test procedure consists of four steps, i.e. first a grease working step which is followed by three consecutive Stribeck step tests. Two grease samples from each of the four grease compositions have undergone the entire test procedure. These duplications were performed to monitor the repeatability of the test between two different tests carried out in the exact same conditions. The same ball and disc used for each of the grease samples were cleaned prior to running of the tests and the test repeat. The tests were run with fresh grease.

[0056] The grease working step had the purpose of ensuring an even distribution of the grease and to prepare the same initial condition for each test, by shearing the grease in the same way and for the same time, before the start of the actual test.

Table 1

	Grease working step (1st step)	Stribeck steps (2nd, 3rd, 4th steps)
Load [N]	1	31
Max Hertz pressure [GPa]	0.31	0.96
Temperature [°C]	60	60
Speed range [mm/s]	5 (constant)	5 - 1000 (in 50 log steps)
SRR [%]	0	10
Time [min]	5	6

[0057] In Table 1, the test operating conditions during the grease working step and the Stribeck test steps are shown.

[0058] In the four test procedure steps, the following operating conditions were applied:

Step 1 - Grease working step: a ball load of 1 N was applied on the disc resulting in Hertzian contact pressure of 0.31 GPa, and a constant speed of 5 mm/s, for 5 minutes.

Steps 2-4 - The three consecutive Stribeck steps: a ball load of 31 N was applied on the disc resulting in a Hertzian contact pressure of 1 GPa, and the speed increased from 5 mm/s to 1000 mm/s at a slide-to-roll ratio (SRR) of 10 %. This step was repeated three times to monitor the repeatability of the step within the same test, and to analyse the friction coefficient evolution after each step due to the grease thixotropic character.

[0059] A test sample 1 according to the present invention was manufactured from a paraffinic mineral blend base oil of 120 cSt from Scharr, Tunap, and 10wt.% calciumhydroxystearate from Barlocher, 2 wt.% calciumstearate from Barlocher, 3 wt.% aerosol from Evonik i.e. hydrophilic silicon oxide primary particles having a BET specific surface area of 175-220 m²/g and the primary particle size ranges typically between 7-25 nm, 1.2 wt.% triphenylphosphate from M. Volkholz, 2 wt.% disodiumsebacic acid from M. Volkholz, 0.5 wt.% alkylphosphateamine from Ciba, 0.5 wt.% from butylated triphenyl phosphorothionate from Ciba, 0.5 wt.% benzotriazole from Ciba, 2.5 wt.% triphenylphosphorothionate from Ciba, 2 wt.% ditterdodecylpolysulfide from Elf Atochem, 5 wt.% dioctylsebacicacid-acid ester from Croda and 5 wt.% glyceryl isostearate from Croda. The grease has been composed by adding, mixing and milling in a 3-roller-mill for 30 minutes in total.

[0060] For comparison reasons, test sample 1 of the present invention was compared with three reference greases of the following compositions:

- (a) Li-1 comprising of lithium salts as a grease thickener, and having a mineral base oil viscosity of 100 mm²/s at 40 °C;
- (b) Li-2 comprising lithium salts as a grease thickener, and a mineral base oil viscosity of 200 mm²/s at 40 °C;

(c) CaSX-1 comprising calcium sulfonate and calcium salts as a grease thickener, and a base oil blend of mineral and synthetic PAO base oil of a viscosity of 80 mm²/s at 40 °C.

[0061] In Figure 1, the results of the test sample 1 and the three reference grease compositions are compared with each other, whereby the values of the Stribeck friction coefficient [-] and the entrainment speed [mms⁻¹] measurements obtained on the MTM rig are shown. The boundary, mixed and full film lubricating regimes are indicated in the figure over the ranges of entrainment speeds.

[0062] A test sample 2 according to the present invention has been manufactured from a paraffinic mineral blend base oil of 120 cSt from Scharr, Tunap, and 10wt.% calciumhydroxystearate from Barlocher, 2 wt.% calciumstearate from Barlocher, 3 wt.% aerosol from Evonik i.e. hydrophilic silicon oxide primary particles having a BET specific surface area of 175-220 m²/g and the primary particle size ranges typically between 7-25 nm, 1.2 wt.% triphenylphosphate from M. Volkholz, 2 wt.% disodiumsebacic acid from M. Volkholz, 0.5 wt.% alkylphosphateamine from Ciba, 0.5 wt.% from butylated triphenyl phosphorothionate from Ciba, 0.5 wt.% benzotriazole from Ciba, 2.5 wt.% triphenylphosphorothionate from Ciba, 2 wt.% ditertdodecylpolysulfide from Elf Atochem, 10 wt.% glyceryl isostearate ester from Croda. The grease has been composed by adding, mixing and milling in a 3-roller-mill for 30 minutes in total.

[0063] For comparison reasons, test sample 2 of the present invention was compared with three reference greases of the following compositions:

- (a) Li-1 comprising of lithium salts as a grease thickener, and having a mineral base oil viscosity of 100 mm²/s at 40 °C;
- (b) Li-2 comprising lithium salts as a grease thickener, and a mineral base oil viscosity of 200 mm²/s at 40 °C;
- (c) CaSX-1 comprising calcium sulfonate and calcium salts as a grease thickener, and a base oil blend of mineral and synthetic PAO base oil of a viscosity of 80 mm²/s at 40 °C.

[0064] In Figure 2, the results of the test sample 2 and the three reference grease compositions are compared with each other, whereby the values of the Stribeck friction coefficient [-] and the entrainment speed [mms⁻¹] measurements obtained on the MTM rig are shown. The boundary, mixed and full film lubricating regimes are indicated in the figure over the ranges of entrainment speeds.

[0065] A test sample 3 according to the present invention has been manufactured from a paraffinic mineral blend base oil of 120 cSt from Scharr, Tunap, and 10wt.% calciumhydroxystearate from Barlocher, 2 wt.% calciumstearate from Barlocher, 3 wt.% aerosol from Evonik i.e. hydrophilic silicon oxide primary particles having a BET specific surface area of 175-220 m²/g and the primary particle size ranges typically between 7-25 nm, 1.2 wt.% triphenylphosphate from M. Volkholz, 2 wt.% disodiumsebacic acid from M. Volkholz, 0.5 wt.% alkylphosphateamine from Ciba, 0.5 wt.% from butylated triphenyl phosphorothionate from Ciba, 0.5 wt.% benzotriazole from Ciba, 2.5 wt.% triphenylphosphorothionate from Ciba, 2 wt.% ditertdodecylpolysulfide from Elf Atochem, and 10 wt.% dioctylsebacicacid-acid ester from Croda. The grease has been composed by adding, mixing and milling in a 3-roller-mill for 30 minutes in total.

[0066] For comparison reasons, test sample 3 of the present invention was compared with three reference greases of the following compositions:

- (a) Li-1 comprising of lithium salts as a grease thickener, and having a mineral base oil viscosity of 100 mm²/s at 40 °C;
- (b) Li-2 comprising lithium salts as a grease thickener, and a mineral base oil viscosity of 200 mm²/s at 40 °C;
- (c) CaSX-1 comprising calcium sulfonate and calcium salts as a grease thickener, and a base oil blend of mineral and synthetic PAO base oil of a viscosity of 80 mm²/s at 40 °C.

[0067] In Figure 3, the results of the test sample 3 and the three reference grease compositions are compared with each other, whereby the values of the Stribeck friction coefficient [-] and the entrainment speed [mms⁻¹] measurements obtained on the MTM rig are shown. The boundary, mixed and full film lubricating regimes are indicated in the figure over the ranges of entrainment speeds.

[0068] From Figures 1-3, it will be clear that that the test samples 1-3 in accordance with the present invention constitute an improvement in terms of lubrication and friction when compared with the three reference grease compositions.

Claims

1. A non-hydroxide grease composition containing less than 0.2% by weight of metal hydroxide, based on the total weight of the grease composition, which grease composition comprises a base oil and a thickener which comprises amorphous hydrophilic fumed silicon oxide particles, a calcium salt of 12-hydroxy stearic acid and one or more esters that contain at least one OH group, wherein the amount of the ester(s) is 0.1-20% by weight, based on the total amount of the grease composition, wherein the amorphous hydrophilic fumed silicon oxide particles have a

BET specific surface area of at least 10 m²/g and at least 80% of the amorphous hydrophilic fumed silicon oxide particles have a particle size in the range of from 5-50 nm, and wherein the amount of the thickener is in the range of from 0.1-40% by weight, based on the total weight of the grease composition.

- 5 2. A grease composition according to claim 1, wherein the one or more esters contain two or more unsaturated C-C bonds.
3. A grease composition according to claim 1 or 2, wherein the one or more esters are diesters.
- 10 4. A grease composition according to any one of claims 1-3, wherein the one or more esters are esterified fatty acids.
5. A grease composition according to any one of claims 1-4, comprising in addition one or more sulphonates, sulphates, phosphates and/or phosphonates.
- 15 6. A method for manufacturing a grease composition according to any one of claims 1-5, which method comprises mixing the base oil, the amorphous hydrophilic fumed silicon oxide particles, the calcium salt of 12-hydroxy stearic acid and the one or more esters that contain at least one OH group in any possible order of sequence and subjecting before or after mixing the amorphous hydrophilic fumed silicon oxide particles, the calcium salt of 12-hydroxy stearic acid and the one or more esters that contain at least one OH group to a mechanical treatment, a thermal treatment or to both a mechanical treatment and a thermal treatment, wherein the thermal treatment is a heating step which involves heating at a temperature in the range of 30-120°C.
- 20 7. Use of a grease composition according to any one of claims 1-5 for lubricating a bearing, a gearing or a coupling.

Patentansprüche

- 30 1. Hydroxidfreie Schmierfettzusammensetzung, die weniger als 0,2 Gew.-% Metallhydroxid, bezogen auf das Gesamtgewicht der Schmierfettzusammensetzung, enthält, wobei die Schmierfettzusammensetzung ein Grundöl und ein Verdickungsmittel, das amorphe hydrophile pyrogene Siliciumoxidpartikel, ein Calciumsalz von 12-Hydroxystearinsäure und einen oder mehrere Ester, die mindestens eine OH-Gruppe enthalten, umfasst, umfasst, wobei die Menge des Esters bzw. der Ester 0,1-20 Gew.-% bezogen auf die Gesamtmenge der Schmierfettzusammensetzung, beträgt, wobei die amorphen hydrophilen pyrogenen Siliciumoxidpartikel eine spezifische BET-Oberfläche von mindestens 10 m²/g aufweisen und mindestens 80 % der amorphen hydrophilen pyrogenen Siliciumoxidpartikel eine Partikelgröße im Bereich von 5-50 nm aufweisen und wobei die Menge des Verdickungsmittels im Bereich von 0,1-40 Gew.-%, bezogen auf das Gesamtgewicht der Schmierfettzusammensetzung, liegt.
- 35 2. Schmierfettzusammensetzung nach Anspruch 1, wobei der eine oder die mehreren Ester zwei oder mehr ungesättigte C-C-Bindungen enthalten.
- 40 3. Schmierfettzusammensetzung nach Anspruch 1 oder 2, wobei es sich bei dem einen oder den mehreren Estern um Diester handelt.
- 45 4. Schmierfettzusammensetzung nach einem der Ansprüche 1-3, wobei es sich bei dem einen oder den mehreren Estern um veresterte Fettsäuren handelt.
5. Schmierfettzusammensetzung nach einem der Ansprüche 1-4, die zusätzlich ein oder mehrere Sulfonate, Sulfate, Phosphate und/oder Phosphonate umfasst.
- 50 6. Verfahren zur Herstellung einer Schmierfettzusammensetzung nach einem der Ansprüche 1-5, bei dem man das Grundöl, die amorphen hydrophilen pyrogenen Siliciumoxidpartikel, das Calciumsalz von 12-Hydroxystearinsäure und den einen oder die mehreren Ester, die mindestens eine OH-Gruppe enthalten, in einer beliebigen möglichen Reihenfolge mischt und die amorphen hydrophilen pyrogenen Siliciumoxidpartikel, das Calciumsalz von 12-Hydroxystearinsäure und den einen oder die mehreren Ester, die mindestens eine OH-Gruppe enthalten, vor oder nach dem Mischen einer mechanischen Behandlung, einer Wärmebehandlung oder sowohl einer mechanischen Behandlung als auch einer Wärmebehandlung unterwirft, wobei es sich bei der Wärmebehandlung um einen Erhitzungsschritt handelt, der ein Erhitzen auf eine Temperatur im Bereich von 30-120 °C umfasst.
- 55

7. Verwendung einer Schmierfettzusammensetzung nach einem der Ansprüche 1-5 zum Schmieren eines Lagers, eines Getriebes oder einer Kupplung.

5 **Revendications**

1. Composition de graisse sans hydroxyde contenant moins de 0,2 % en poids d'hydroxyde métallique, relativement au poids total de la composition de graisse, ladite composition de graisse comprenant une huile de base et un épaississant qui comprend des particules d'oxyde de silicium amorphe hydrophile pyrogéné, un sel de calcium de l'acide 12-hydroxystéarique et un ou plusieurs esters qui contiennent au moins un groupe OH, dans laquelle la quantité du ou des esters est de 0,1 à 20 % en poids, relativement à la quantité totale de la composition de graisse, dans laquelle les particules d'oxyde de silicium amorphe hydrophile pyrogéné ont une surface spécifique BET d'au moins 10 m²/g et au moins 80 % des particules d'oxyde de silicium amorphe hydrophile pyrogéné ont une taille de particule de 5 à 50 nm, et dans laquelle la quantité de l'épaississant est de 0,1 à 40 % en poids, relativement au poids total de la composition de graisse.
2. Composition de graisse selon la revendication 1, dans laquelle lesdits un ou plusieurs esters contiennent deux liaisons C-C insaturées ou plus.
3. Composition de graisse selon la revendication 1 ou 2, dans laquelle lesdits un ou plusieurs esters sont des diesters.
4. Composition de graisse selon l'une quelconque des revendications 1 à 3, dans laquelle lesdits un ou plusieurs esters sont des acides gras estérifiés.
5. Composition de graisse selon l'une quelconque des revendications 1 à 4, comprenant en outre un ou plusieurs sulfonates, sulfates, phosphates et/ou phosphonates.
6. Procédé de fabrication d'une composition de graisse selon l'une quelconque des revendications 1 à 5, ledit procédé comprenant un mélange de l'huile de base, des particules d'oxyde de silicium amorphe hydrophile pyrogéné, du sel de calcium de l'acide 12-hydroxystéarique et desdits un ou plusieurs esters qui contiennent au moins un groupe OH, dans n'importe quel ordre de séquence possible, et, avant ou après le mélange, une soumission des particules d'oxyde de silicium hydrophile amorphe pyrogéné, du sel de calcium de l'acide 12-hydroxystéarique et desdits un ou plusieurs esters qui contiennent au moins un groupe d'OH, à un traitement mécanique, à un traitement thermique ou à la fois à un traitement mécanique et à un traitement thermique, dans lequel le traitement thermique est une étape de chauffage qui comprend un chauffage à une température de 30 à 120 °C.
7. Utilisation d'une composition de graisse selon l'une quelconque des revendications 1 à 5 pour lubrifier un roulement, un engrenage ou un accouplement.

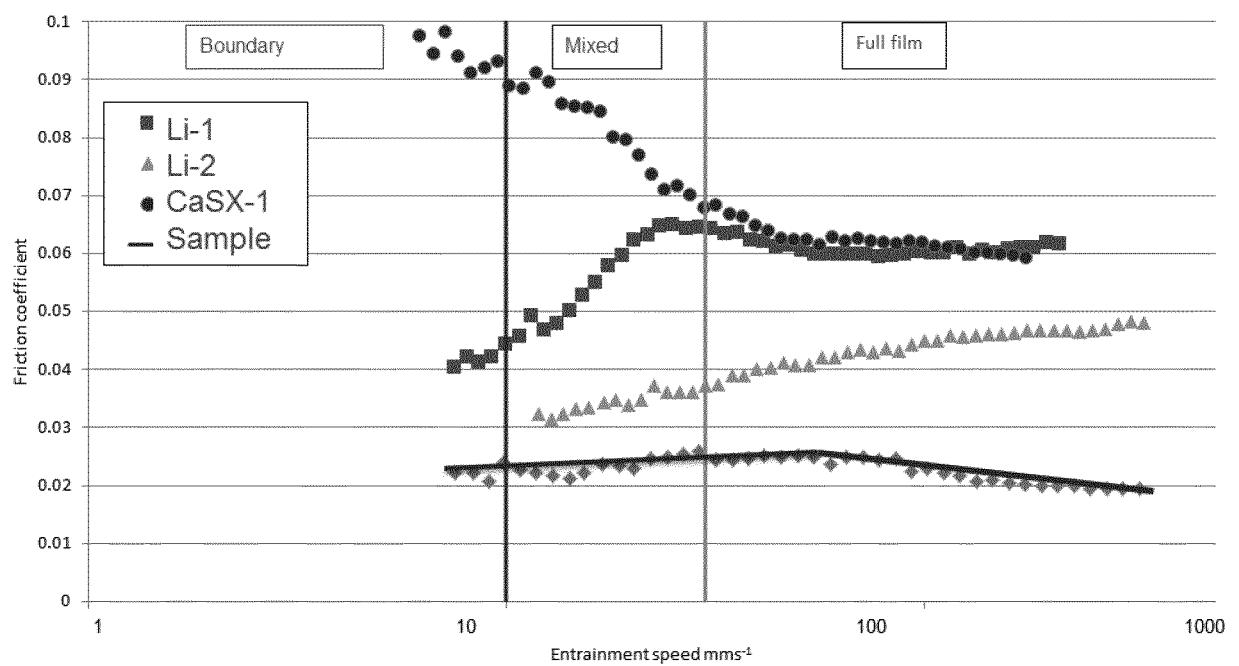


Figure 1

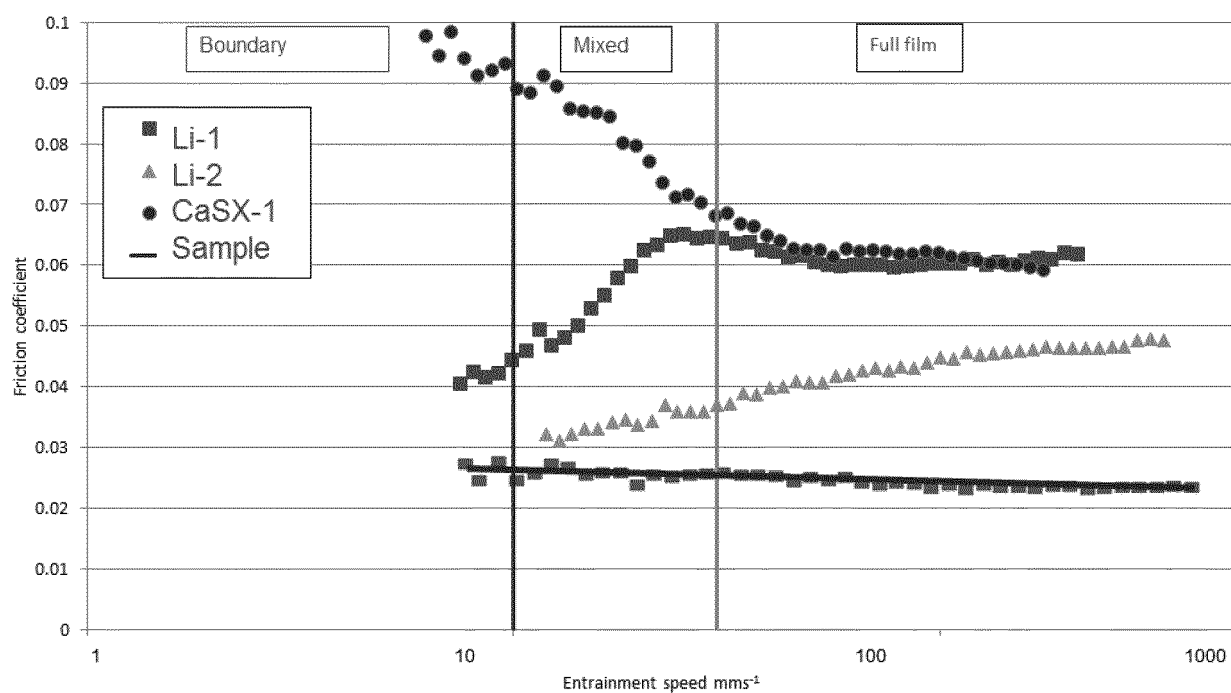


Figure 2

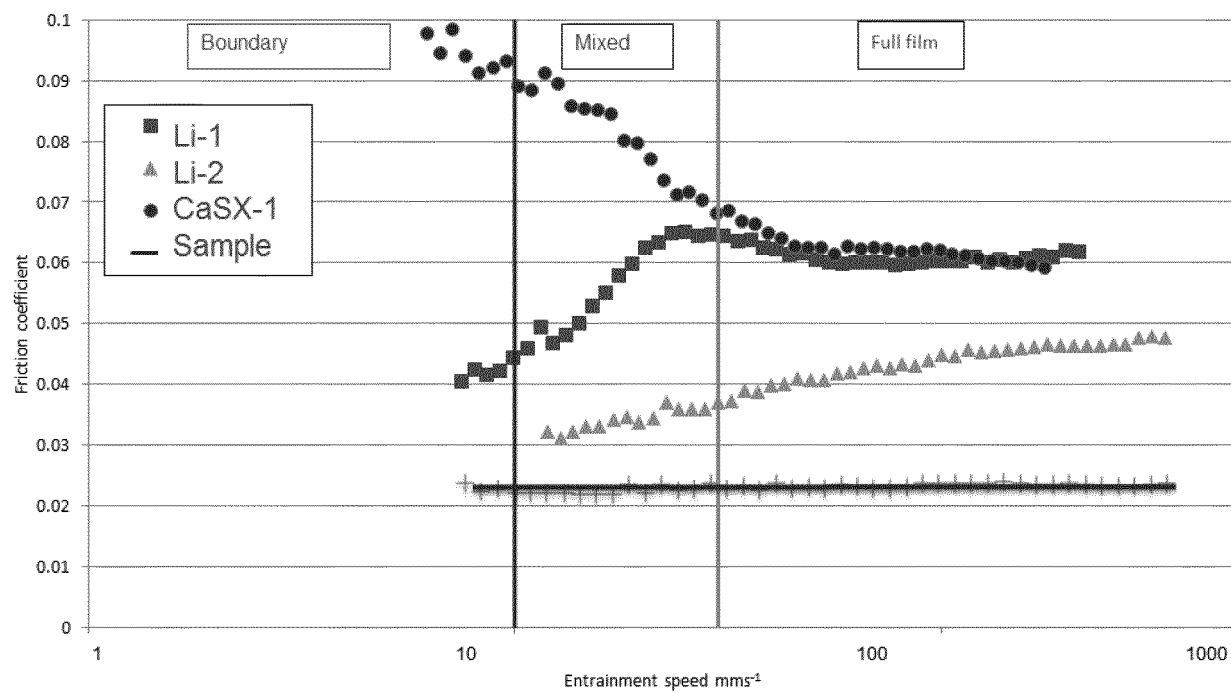


Figure 3

REFERENCES CITED IN THE DESCRIPTION

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