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(54) **GREASE COMPOSITION**

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(57) **ABSTRACT**

The disclosure relates to a grease composition comprising:

(A) a synthetic base oil in majority consisting of alkylaromatic(s);

(B) a thickener in majority consisting of at least one metal soap of fatty acids; and

(C) a solid lubricant in majority consisting of nanoparticulate polytetrafluorethylene, at least 85% of the particles of which have a size of less than one micron.

GREASE COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a National Phase Entry of International Application No. PCT/IB2010/050851, filed on Feb. 26, 2010, which claims priority to French application Ser. No. 09/00898, filed on Feb. 27, 2009, both of which are incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention relates to grease compositions, in particular which may be used for greasing rolling bearings.

BACKGROUND

[0003] There exist many applications where liquid lubricants are not suitable because they "drift" relatively to the greasing point. These are in particular rolling and sliding bearings, open gears, metal cables and chain drives, and more generally applications which do not include any sealing system. For these applications, lubricant greases are used, which are solid or semi-fluid substances resulting from the dispersion of a thickener in a liquid lubricant, integrating additives which give them particular properties.

[0004] The very large majority of lubricant greases are prepared with thickeners of the fatty acid metal salt type. The fatty acid is dissolved in the base oil at a relatively high temperature, and then the suitable metal hydroxide is added. After having evaporated the water by baking, which is formed during the reaction, it is cooled during a defined period of time in order to form the soap lattice.

[0005] Lithium, sodium, calcium, barium, titanium or aluminium hydroxides are suitable as metal compounds for making the grease. Fatty acids with a long chain of the order of C_{14} to C_{28}, mainly C_{18}, are generally derived from vegetable oils (castor oil for example) or animal oils (for example tallow). They may be hydrogenated. The most known derivative is 12-hydroxystearic acid derived from ricinoleic acid. It is also possible to use, in combination with fatty acids with a long chain, short chain acids, typically comprising between 6 and 12 carbon atoms, such as for example azelaic acid, ... So-called complex greases are then formed.

[0006] The soaps form a fibrous structure which retains the lubricant oil. Aluminium soaps, them, have a spherical gel structure. Other inorganic thickeners such as for example bentonite, silica gel may be used. Polycarbamides (polyureas) are also found among the thickeners. These thickeners are generally used for special applications, for example high temperature greases.

[0007] For certain applications, for example for lubricated rolling bearings, but also for machine tool slide rails, or for centralized greasing systems in automobiles, transmissions, it is desirable that the greases have a low friction coefficient, so as to increase the yield of the systems and possibly generate savings in fuel (so-called "ecofuel" or "fuel saving" properties). These greases should further remain sufficiently consistent so as not to run out of the greasing point, and play their role of reducing wear and preventing seizing.

[0008] Patent application JP 55082196 discloses certain grease compositions incorporating as additives, solid lubricants in particulate form in order to improve the friction coefficient and to prevent seizing of the systems. It is known that solid lubricants, in particular polytetrafluoroethylene (PTFE), should be incorporated into the greases at high contents, above 5% or further 10% by mass, sometimes up to 40% by mass, so that an effect is noticed.

[0009] It is also known that anti-friction and anti-wear properties of these particulate solids are improved when the particles are of nanometric size. Patent application WO 2008/069936 thus discloses the use of solid lubricants in the form of nanoparticles with a diameter of less than 500 nm in liquid lubricants or in greases, in order to improve their anti-wear and lubrication properties. The amounts of solid lubricants required for obtaining a significant effect are still however very substantial, of the order of 20% by mass, greater than 15% by mass. This poses problems of cost of the formulations, and such a high content may also spoil other properties of the lubricants and of the greases, notably having an effect on their viscosity, or on their consistency as regards greases.

[0010] Such nanoparticulate solid lubricants, for example in polytetrafluorethylene (PTFE), may also be incorporated in motor oils, in order to increase their lubricating power, for example at contents comprised between 0.01 and 10% by mass, in combination with compounds of the organomolybdenum, zinc dithiophosphate, boron compound type, . . . as described in patent application US 2005/0124504. However, it seems that the whole of the parameters with which a maximum antifriction effect of the solid nanoparticles in the lubricants or in the greases may be attained, has not been adjusted in the prior art, in particular the parameters which determine the more or less proper dispersion of these particular solids in said lubricants or grease. These parameters may prove to be substantially different from one medium to the other, for example between a grease and a liquid lubricant, and depend on the respective nature of the particles, of the bases, of the thickeners used.

[0011] Therefore there in particular exists a need for grease compositions where the anti-friction effect of the solid nanoparticles is improved. Accessorily, there exists a need for such greases also having an improved anti-wear effect. Surprisingly, the applicant noticed that a grease having a specific combination of synthetic base oil, of fatty acid metal soaps and of additives of the solid lubricant type in nanoparticulate form, had very low friction coefficients, expressed by very high yields on lubricated rolling bearing systems.

SUMMARY

[0012] The present invention relates to grease compositions comprising:

- **[0013]** at least one synthetic base oil of the alkylaromatic type,
- **[0014]** one or more fatty acid metal soaps,
- **[0015]** a solid lubricant consisting of nanoparticulate polytetrafluoroethylene where at least 80% of the particles have a size of less than one micron.

[0016] An advantage of the invention is the obtaining of significant ant-friction effects with low amounts of solid nanoparticles, typically less than or equal to 10% by mass, or further less than or equal to 5% by mass of nanoparticles based on the total weight of the compositions. Thus, an economical means is found for producing grease compositions with a low friction coefficient, which may therefore lead to high yields on rolling systems, or allow savings in energy on various systems, for example transmissions, in particular automobile transmissions or constant-velocity universal joints.

[0017] Another advantage of the invention is that this effect may be obtained with inexpensive and available conventional thickeners which are metal soaps of fatty acids. Certain thickeners, for example polyureas, are expensive, difficult to make and not accessible in large amounts. These soaps further have the advantage of a very good mechanical strength, comparatively with other thickeners, for example polyureas. Thus, the greases according to the invention do not lose their structure when they are subject to mechanical stresses, and may be used in applications where no sealing system is provided, without any fear of leaks out of the greasing point.

[0018] The invention relates to a grease composition comprising:

- **[0019]** (A) a synthetic base oil in majority consisting of alkylaromatic(s) (A1),
- **[0020]** (B) a thickener in majority consisting of at least one fatty acid metal soap,
- **[0021]** (C) a solid lubricant in majority consisting of nanoparticulate polytetrafluoroethylene, at least 85% of the particles of which have a size of less than one micron.

[0022] The oil in the form of alkylaromatics (A1) preferably makes up at least 80% by weight of the base oil (A) in said composition. The metal soap(s) (B) preferably makes up at least 80% by weight of the thickener (B) in said composition. The solid lubricant (C) preferably consists of at least 80%, notably at least 90% by weight of nanoparticulate polytetrafluoroethylene.

[0023] According to an embodiment, a solid lubricant (C) only consists of nanoparticulate polytetrafluoroethylene. Preferably, the thickener (B) is free of urea compounds. Preferably, the composition is free of calcium carbonate. Preferably, it comprises from 0.1 to 10% by weight, notably 2 to 7% by weight of solid lubricant in the form of nanoparticulate polytetrafluoroethylene. Preferably the polytetrafluorethylene particles have an average size comprised between 150 and 800 nm. The synthetic base oils may be selected from oils of the alkyl benzene or alkyl naphthalene type.

[0024] According to an embodiment, the synthetic base oil (A) comprises at least one other mineral, synthetic or natural base oil (A2), preferably a synthetic oil selected from polyalphaolefins. Preferably, the soaps are simple metal soaps of either saturated or not, either hydroxylated or not, fatty acids comprising from 14 to 28 carbon atoms, or complex metal soaps of one or more either saturated or not, either hydroxylated or not, fatty acids comprising from 14 to 28 carbon atoms, in combination with one or more carboxylic acids with a short hydrocarbon chain comprising from 6 to 12 carbon atoms.

[0025] The metal soaps of fatty acids may be selected from titanium, aluminium soaps or from those of alkaline and earth alkaline metals, preferably, lithium, calcium, sodium, barium. The composition according to the invention may comprise one or more anti-wear and/or extreme pressure agents.

[0026] The invention also relates to a grease composition which comprises, based on the total weight of the composition:

- **[0027]** from 50 to 90% by weight of the synthetic base oil (A),
- **[0028]** from 1 to 15% by weight of the thickener (B) in majority consisting of at least one metal soap of fatty acids,
- **[0029]** from 0.1 to 10% by weight of solid lubricant (C) in the form of nanoparticulate polytetrafluoroethylene powder with at least 85% of the particles having a size of less than one micron,
- **[0030]** from 0 to 10% of one or more anti-wear and/or extreme pressure additives.

[0031] Preferably, the composition comprises 5 to 15% by weight, based on the total weight of the composition, of a synthetic oil (A2) of the polyalphaolefin type. Preferably, the composition has a base oil (A) having a kinematic viscosity at 40° C., measured according to the ASTM D 445 standard, comprised between 10 and 120 mm^2/s. Preferably, the composition has a consistency according to the ASTM D217 standard of more than 265, preferably comprised between 265 and 475, or between 265 and 295, or between 310 and 340, or between 335 and 385 tenths of millimeters, or in that it has a consistency according to the ASTM D217 standard of more than 400 tenths of millimeters, preferably comprised between 400 and 475 or between 445 and 475 tenths of millimeters.

[0032] The invention also relates to a method for preparing a grease as defined above and which comprises the following steps:

[0033] dissolving one or more fatty acids in a fraction of the base oil or of the base oil mixture,

[0034] adding metal compounds, preferably of the type: metal oxide, hydroxide or carbonate or lime,

[0035] saponifying the fatty acids with said metal compounds,

[0036] incorporating nanoparticulate polytetrafluorethylene, at least 85% of the particles of which have a size of less than one micron.

[0037] The invention also relates to the use of the grease composition as defined above as a grease for transmissions, in particular automobile transmissions. The invention also relates to the use of the grease composition as defined above as a grease for lubricated rolling bearings, machine tool slide rails or centralized greasing systems in automobiles.

[0038] By "in majority consisting of" is meant in the present text that the content of this compound is of at least 50% by weight of the targeted compound. The content in question may also attain at least 80%, preferably at least 85 or 90 or 95% by weight, or even substantially 100% by weight of the targeted compound.

DETAILED DESCRIPTION

[0039] Base Oils:

[0040] The grease compositions according to the invention contain at least one synthetic base oil of the alkylaromatic type. These oils are obtained by alkylation of aromatic compounds with compounds such as olefins, monohalogenated or monohydroxylated paraffins, or other alkylation agents, in the presence of an acid catalyst, for example of the Friedel-Craft type or zeolites. The aromatic compounds may for example be benzene, naphthalene or anthracene, optionally substituted. The alkyl benzene or alkyl naphthalene bases are preferred.

[0041] The resulting alkylaromatic synthetic bases may be mono- or polyalkylaromatics, for example di- or tri-alkylaromatics (for example mono-, di-, tri- or poly-alkyl benzene or naphthalene or anthracene). The alkyl substituents may be linear or branched and preferably include from 9 to 24 carbon atoms, preferentially from 12 to 24 carbon atoms. The presence of substituents including less than 9, or less than 12 carbon atoms may lead, notably in bases of the alkyl benzene type, to compounds which are too volatile, and the substituents including more than 24 carbon atoms provide too high viscosity for the target applications.

[0042] These different compounds may be present either alone or as a mixture in the greases according to the invention. They have a strong solvent power which should contribute to optimum dispersion of the additives in the compositions according to the invention. The kinematic viscosity at 40° C. according to ASTM D445 of these alkyklaromatic synthetic bases is preferentially comprised between 10 and 120 cSt.

[0043] When applications such as lubricated bearings or centralized greasing for automobiles are targeted, bases will be preferred for which the kinematic viscosity at 40° C. according to ASTM D445 is comprised between 10 and 80 cSt, preferentially between 10 and 50 cSt, preferentially between 20 and 40 cSt, so as to guarantee good operability, good pumpability, and good cold properties, allowing use down to −20° C., or even down to −40° C. When applications such as transmissions are targeted, bases will be preferred for which the kinematic viscosity at 40° C. according to ASTM D445 is comprised between 70 and 110 cSt, preferentially between 30 and 40 cSt, preferentially between 35 and 37 cSt, so as to guarantee an adequate oil film under higher loads. These alkylaromatic bases are preferably present at contents comprised between 50 and 90% by weight, preferentially between 65 and 85% or between 70 and 80% in the grease compositions according to the invention.

[0044] Other Base Oils:

[0045] The grease compositions according to the invention may contain in addition to the alkylaromatic synthetic bases described above, other base oils in a lesser amount. The other base oil(s) used in the compositions according to the present invention may be oils of mineral or synthetic origin of the groups I to VI according to the classes defined in the API (American Petroleum Institute) classification.

[0046] The mineral base oils according to the invention include all types of bases obtained by atmospheric and vacuum distillation of crude oil, followed by refining operations such as extraction with a solvent, de-asphalting, dewaxing with a solvent, hydrotreatment, hydrocracking and hydro-isomerization, hydrofinishing. The base oils of the grease compositions according to the present invention may also be synthetic oils, such as certain esters, silicones, glycols, polybutene, polyalphaolefins (PAOs). The base oils may also be oils of natural origin, for example esters of alcohol and carboxylic acids which may be obtained from natural resources such as sunflower, rapeseed, palm oil, ...

[0047] Preferentially, synthetic oils of the polyalphaolefin (PAO) type combined with alkylaromatic synthetic bases as described above are used in the compositions according to the invention. The polyalphaolefins are for example obtained from monomers having from 4 to 32 carbon atoms (for example octene, decene). Their average weight molecular mass is typically comprised between 250 and 3,000.

[0048] Mixtures of synthetic and mineral oils may also be used. Preferably the base oils other than the alkylaromatic synthetic bases described above, are present at contents comprised between 5 and 15% in the compositions according to the invention. The kinematic viscosity at 40° C. according to ASTM D445 of the base oil or of the base oil mixture used in the compositions according to the invention is preferentially comprised between 10 and 120 cSt.

[0049] When applications such as lubricated bearings or centralized greasing for automobiles are targeted, a base oil or a base oil mixture will be preferred, for which the kinematic viscosity at 40° C. according to ASTM D445 is comprised between 10 and 80 cSt, preferentially between 10 and 50 cSt, preferentially between 20 and 40 cSt, so as to guarantee good operability, good pumpability, and good cold properties, allowing use down to −20° C., or even down to −40° C. When applications such as transmissions are targeted, a base oil or a base oil mixture will be preferred, the kinematic viscosity of which at 40° C. according to ASTM D445 is comprised between 70 and 110 cSt, preferentially between 30 and 40 cSt, preferentially between 35 and 37 cSt, so as to guarantee an adequate oil film under higher loads.

[0050] Thickeners:

[0051] The greases according to the invention are thickened with metal soaps of fatty acids, which may be prepared separately or in situ during the making of the grease (in the latter case, the fatty acid is dissolved in the base oil and the suitable metal hydroxide is then added). These thickeners are easily available and inexpensive products currently used in the field of greases. Moreover, the thereby thickened greases have very good mechanical stability, for example comparatively with greases based on polyureas, this allows them to be easily used in applications where the grease is found in a non-confined enclosure.

[0052] Long chain fatty acids are preferentially used, typically comprising from 10 to 28 carbon atoms, either saturated or unsaturated, optionally hydroxylated. The long chain fatty acids (typically comprising from 10 to 28 carbon atoms) are for example, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, oleic, linoleic, erucic acids and their hydroxylated derivatives. 12-hydroxystearic acid is the most well-known derivative of this category, and preferred. These long chain fatty acids generally derive from vegetable oils, for example palm, castor, rapeseed, sunflower oil . . . or from animal fats (tallow, whale oil . . .).

[0053] So-called simple soaps may be formed by using one or more long chain fatty acids. It is also possible to form so-called complex soaps by using one or more long chain fatty acids in combination with one or more carboxylic acids with a short hydrocarbon chain comprising at most 8 carbon atoms.

[0054] The saponification agent used for making the soap may be a metal compound of lithium, sodium, calcium, barium, titanium, aluminium, preferentially lithium and calcium, and preferably a hydroxide, oxide or carbonate of these metals. One or more metal compounds may be used, either having the same metal cation or not, in the greases according to the invention. It is thereby possible to associate lithium soaps combined with calcium soaps in a lesser proportion.

[0055] The metal soaps are used at contents of the order of 1 to 15% by weight, preferentially from 2 to 10% or further from 4 to 10% or from 4.5 to 6% by weight in the greases according to the invention. When applications such as lubricated bearings or centralized greasing for automobiles are targeted, the use of 1 to 6%, preferentially 2 to 5% of metal soap(s) will be preferred, so as to obtain fluid or semi-fluid greases of grade 000 or 00 according to the NLGI classification. When applications such as transmissions are targeted, the use of 6.5% to 15%, preferentially 7 to 13% or 8 to 12% of metal soap(s) will be preferred, so as to obtain greases of grade 0, grade 1 or grade 2 according to the NLGI classification. In every case, these thickener contents are relatively low in the greases according to the invention, so as to obtain greases for which the consistency corresponds to a grade comprised between 000, 00, 0, 1 or 2 according to the NLGI classification, and to promote an increase in the yield, energy savings or an ecofuel effect, for example on systems such as lubricated rolling bearings, centralized greasing systems for vehicles or transmissions.

[0056] Method for Preparing the Greases:

[0057] The greases according to the invention are preferentially made by forming the metal soap in situ. One or more fatty acids are dissolved in a fraction of the base oil or of the base oil mixture at room temperature. This fraction is usually of the order of 40% of the total amount of oil contained in the final grease. The fatty acids may be long acids, comprising from 14 to 28 carbon atoms, in order to form a simple soap, optionally combined with short fatty acids, comprising from 6 to 12 carbon atoms, in order to form complex soaps.

[0058] Metal compounds preferentially of the metal oxide, hydroxide or carbonate type are added at a temperature of about 60° C. Thus, it is possible to add a single type of metal or to combine several metals. The preferred metal of the compositions according to the invention is lithium, optionally combined in a lesser proportion with calcium.

[0059] The saponification reaction of the fatty acids by the metal compounds is left to take place at a temperature of about 80° C. The formed water is then evaporated by baking the mixture at a temperature of about 100 to 200° C. The grease is then cooled by the remaining base oil fraction.

[0060] The nanoparticulate polytetrafluoroethylene and other optional additives are then incorporated at about 80° C. Kneading is then carried out for sufficient time in order to obtain a homogeneous grease composition.

[0061] Grade of the Greases:

[0062] The consistency of a grease measures its hardness or its fluidity at rest. It is evaluated by the penetration depth of a cone of given dimensions and mass. The grease is subject to kneading beforehand. The conditions for measuring the consistency of a grease are defined by the ASTM D 217 standard.

[0063] Depending on their consistency, the greases are distributed in 9 classes or 9 NLGI (National Lubricating Grease Institute) grades frequently used in the field of greases. These grades are indicated in the table below.

NLGI Grade	Consistency according to ASTM D 217 (tenths of millimeters)
000	445-475
00	400-430
0	335-385
1	310-340
2	265-295
3	220-250
4	175-205
5	130-160
6	85-115

[0064] The greases according to the invention have a consistency of more than 265 tenths of millimeters, preferentially comprised between 275 and 475 tenths of millimeters according to the ASTM D217 standard. Preferentially they are of NLGI grade 000, 00, 0, 1 or 2, i.e. their consistency is respectively comprised between 445 and 475, or between 400 and 300, or between 335 and 385, or between 310 and 340, or between 265 and 295 tenths of millimeters according to ASTM D217.

[0065] When applications such as lubricated bearings or centralized greasing for automobiles are targeted, the greases according to the invention are preferentially fluid or semi-fluid greases, with a consistency of, more than 400 tenths of millimeters, preferentially comprised between 400 and 475 tenths of millimeters according to ASTM D217. Preferentially, they are of NLGI grade 00 or 000, i.e. their consistency is respectively comprised between 400 and 430, or 445 and 475 tenths of millimeters according to ASTM D217.

[0066] When applications such as transmission, constant-velocity universal joints are targeted, the greases according to the invention are preferentially fluid or semi-fluid greases with a consistency of more than 265 tenths of millimeters, preferentially comprised between 265 and 335 tenths of millimeters according to ASTM D217. Preferentially, they are of NLGI grade 0, 1 or 2, i.e. their consistency is respectively comprised between 335 and 385, or 310 and 340, or 265 and 295 tenths of millimeters according to ASTM D217. Generally, the greases according to the invention tend to be more fluid than the average of the greases used in the relevant applications, so as to promote an increase in the yield, energy savings or an “ecofuel” effect for example on systems such as lubricated rolling bearings, centralized greasing systems for vehicles or transmissions.

[0067] PTFE Nanoparticles:

[0068] The greases according to the invention contain nanoparticulate polytetrafluoroethylene (PTFE). This PTFE may be added in the dry powder condition or else in the form of a concentrated dispersion, wherein the powder is dispersed in a pre-dilution lubricant oil, for example a synthetic oil of the polyalkylaromatic oil or PAO type as described above. The term of nanoparticulate PTFE designates a powder or a dispersion of powder in an oil, wherein at least 85%, preferentially at least 90%, still more preferentially at least 95% (in number) of the particles have a size of less than one micron. More preferably, 100% of the number of particles has a size of less than one micron.

[0069] In the whole present text, the measurement of the size of the PTFE nanoparticles is accomplished according to the teaching of patent application WO 2004/067608 (corresponding to patent application EP 1 594 682). Reference will be made to the description of the measurements indicated in the application WO 2004/067608 more particularly:

[0070] to the passage of page 16, line 15 to page 17, line 13 for a dry measurement

[0071] to the passage of page 17, line 14 to page 20, line 4 for a measurement in isopropyl alcohol (IPA),

[0072] to the passage of page 20, line 5 to page 22, line 4 for a measurement in an oily medium, a measurement method which is preferred within the scope of the present invention,

[0073] to the passage of page 22, line 5 to page 24, line 4 for a measurement in water.

[0074] Preferentially, at least 80%, or at least 80%, or even 95% in number, or even more preferentially 100% of the PTFE particles in these powders or dispersions have a size of more than 50 nm, preferentially more than 100 nm. The presence of too small particles may create problems of re-aggregation of the particles with each other and penalize their dispersion in the grease. The nanoparticulate PTFE of the greases according to the invention preferably has an average size comprised between 150 and 800 nm, or further between

200 and 700 nm or further between 400 and 600 nm. By average size is meant the average of the distribution of the sizes of particles.

[0075] As indicated above, this nanometric PTFE may be prepared from methods described in the aforementioned patent application EP 1 594 682. Such powders or dispersions are marketed by Shamrock in the Nanoflon® range. The distribution of the particle sizes of the powders or dispersions of PTFE used in the grease compositions according to the invention are measured with an analyzer of the Malvern type, according to suitable methods described in the aforementioned patent application WO 2004/067608 (EP 1 594 682).

[0076] For facilitating the application of the mixture, incorporation of the PTFE nanoparticles as dispersions will be preferred, preferentially in synthetic oils of the alkylaromatic or PAO type, as described above. When a dispersion is used, it forms a concentrate wherein the PTFE particles preferably account for about 20 to 50% by weight, preferentially 25 to 35% by weight or further 30% by weight of the dispersion. The nanometric PTFE is preferably present in the grease compositions according to the invention at contents comprised between 0.1 and 10%, preferentially between 2 and 7%, even more preferentially between 3 and 4.5% or further 3 and 5%. One of the advantages of the invention is to allow a significant anti-friction effect with a small amount of nanoparticles.

[0077] The anti-friction properties of PTFE are known. It is also known that this type of solid lubricant has its properties improved when the powders or dispersions containing them consist of nanoparticles. However, it is also important to give the lubricants and greases which contain them improved anti-friction properties, that said nanoparticles are properly dispersed. It seems that with the combination of PTFE nanoparticles with alkylaromatic base oils and fatty acid metal soaps applied in the greases according to the invention it is possible to obtain this good dispersion and consequently excellent yields which have been observed on rolling systems.

[0078] Other Performance Additives:

[0079] Anti-Wear and/or Extreme Pressure Additives

[0080] The grease compositions according to the present invention may contain at least one sulfur, phosphorus or phospho-sulfur anti-wear and/or extreme pressure agent, preferentially present at contents comprised between 0.5 and 5% by weight based on total weight of the composition. As an example of sulfur-containing anti-wear and extreme pressure additives, mention may be made of dithiocarbamates, thiadiazoles, and benzothiazoles, sulfur-containing olefins. The phospho-sulfur anti-wear and extreme pressure additives may for example be in a non-limiting way, thiophosphoric acid, thiophosphorous acid, esters of these acids, their salts, and dithiophosphates.

[0081] The lubricating compositions according to the present invention may also contain phosphorus-containing anti-wear and extreme pressure additives, such as for example alkyl phosphates or alkyl phosphonates, phosphoric acid, phosphorous acid, mono-, di-, and tri-esters of phosphorous acid and of phosphoric acid, and their salts. Other additives: the grease compositions according to the invention may also contain anti-rust additives, such as for example sulfonates . . . (for example calcium, sodium, barium sulfonates), naphthenates (typically zinc naphthenate), salicylates (typically calcium salicylate) or oxidized waxes, antioxidant or anti-corrosion additives . . . . These additives are typically present at contents comprised between 0 and 10%, preferentially between 0.5 and 2% by weight based on the total weight of the composition. Finally, the compositions according to the invention may also contain any type of additives suitable for their use, for example coloring agents, at contents of the order of 0.05 to 0.5%.

EXAMPLES

Example 1

[0082] We have compared the performances of a bicycle wheel hub including a bearing lubricated with different greases, with the performances obtained with a Mavic hub (such as those mounted on bicycle wheels of the Mavic Cosmic type) provided with ball bearings, considered as an up market reference in the field. The lubricated bearing hub used is of the type of those described in patent application EP 1 719 641. The yield of the rolling bearing system Mavic and of the lubricated bearing system is determined on a test bench:

[0083] A bicycle wheel provided with the hub to be tested (a hub with a Mavic ball bearing, or a hub with bearings lubricated with different greases) is driven by a motor, at an initial speed of 70 km/hour, and then during a heating period of 5 minutes at 50 km/hour.

[0084] During the whole duration of the test, a load of 50 kg is applied to it.

[0085] At the initial instant, the power supply of the motor is switched off and then the distance covered before stopping (or seizing) is measured.

[0086] The distance covered before stopping is a relative measurement of the yield of the different rolling bearing systems. It also allows a relative measurement of the anti-friction properties of the different greases used for lubricating the bearing of the hub. The bicycle wheel is the same for all the tested tires, it is provided with a flexible pipe Hutchinson initially inflated at a pressure of 10 bars.

[0087] All the tested greases are greases of grade 000 according to the NLGI classification.

[0088] The grease A is a grease comprising a mineral base oil of group I of the 150 NS type, thickened with a metal soap, lithium 12-hydroxystearate, of NLGI grade 000

[0089] The grease B is a grease comprising a base oil of the polyglycol type also thickened with lithium 12-hydroxystearate, of NLGI grade 000

[0090] The grease C is a grease comprising a base oil of the alkyl benzene type thickened with lithium 12-hydroxystearate, of NLGI grade 000

[0091] The grease D is a grease according to the invention prepared by incorporating polyfluorotetraethylene nanoparticles into the grease C, it is also of NLGI grade 000.

[0092] Grease D' is a grease prepared by incorporating tungsten bisulfide WS_2 nanoparticles into the grease C, it is also of NLGI grade 000.

[0093] The mass compositions of the greases C and D and D' are indicated in Table 1.

TABLE 1

Composition of the greases (in mass %)			
	Grease C Multi ZS EP 000	Grease D 31665	Grease D' 31663
Alkyl benzene synthetic base 5.53 cSt at 100° C.	89.8%	76.9%	87.8%
PAD Base 10 cSt at 100° C.	—	10.0%	—
Lithium 12-hydroxystearate	5.9%	5.1%	5.8%
Anti-wear/Extreme pressure agent	2.2%	1.9%	2.2%
Anti-wear/antioxidant	0.8%	0.7%	0.8%
Anti-rust	1.2%	1.0%	1.2%
Coloring agent	0.1%	0.1%	0.1%
Nanometric PTFE	—	4.3%	—
Nanometric WS2	—	—	2.25%

[0094] The rolling distances d (in meters) of the different tested hubs are grouped in Table 2.

The last indicated distance d is the distance covered before stopping.

TABLE 2

rolling distances											
		Hub with a bearing lubricated by a grease									
Mavic hub		Grease A		Grease B		Grease C		Grease D		Grease D'	
Time (s)	d (m)	time (s)	d (m)	time (s)	d (m)	time (s)	d (m)	time (s)	d (m)	time (s)	d (m)
0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0
3.3	61	3.5	61	3.5	61	3.5	61	3.3	61	3.4	61
7.1	122	7.0	122	7.0	122	7.0	122	6.7	122	6.9	122
10.6	183	10.8	183	10.7	183	10.7	183	10.4	183	10.6	183
14.8	244	15.0	244	14.8	244	14.8	244	14.5	244	14.6	244
19.2	305	19.7	305	19.3	305	19.3	305	18.8	305	19.2	305
24.2	366	25.0	366	24.2	366	24.2	366	23.7	366	24.2	366
30.1	427	31.5	427	30.0	427	29.8	427	29.0	427	29.7	427
36.6	488	39.5	488	36.8	488	36.4	488	35.4	488	36.2	488
44.9	549	52.0	549	45.4	549	44.6	549	42.9	549	44.2	549
57.4	610	67.0	579	58.0	610	56.7	610	52.9	610	55.4	610
75.8	649			76.0	643	74.8	650	77.0	674	73.7	650

[0095] A yield (rolling distance before stopping) which is significantly lower, is noted for the hub with a bearing lubricated with grease A. The yield obtained with the hub with a bearing lubricated by the greases B and C, is of the level of that of the Mavic reference. In grease D', the incorporation of WS_2 nanoparticles does not provide any improvement relatively to the grease C. The performance level of the greases C and D' are strictly identical.

[0096] An excellent yield, greater than that of the Mavic reference, which however forms the up market of the cycling field, and greater than that of the grease C, is obtained with the hub with a bearing lubricated by the grease D according to the invention. The incorporation of PTFE nanoparticles in the grease C leads to notable improvement in its performances.

Example 2

Influence of the Base

[0097] Teflon nanoparticles identical with those used in the grease D according to the invention were added into a grease (E) based on synthetic base oil of the PAO type, thickened with the same lithium metal soap (lithium 12-hydroxystearate). The anti-wear performances in the 4-ball test ASTM D 2266 of the initial PAO+lithium grease (grease E) were compared with those of greases E with nanometric PTFE at 3% and 5% by mass respectively (greases F, G, respectively), as well as with a grease E with 3% of micronic PTFE with an average diameter of 5 μm (grease H).

[0098] The results are grouped in the Table 3 below:

TABLE 3

anti-wear properties				
	E	F	G	H
Solid lubricant	—	3% by mass of nanometric PTFE	5% by mass of nanometric PTFE	3% by mass of micronic PTFE
Wear diameter ASTMD (μm)	830	790	810	530

[0099] The greases E and F, G have performances of identical level: no notable improvement in the anti-wear properties is provided by adding nanometric PTFE into the grease based on PAO. At an equivalent amount, micrometric PTFE provides a larger gain as regards wear. Without having the intention of being bound by any theory, it seems that in a grease thickened with lithium soap, the base oil-nanoparticles interactions lead to a dispersion of the nanoparticles which is less favorable than in the case of the alkyl benzene base-PTFE nanoparticles pair, which may explain that their incorporation does not give rise to any improvement in the anti-wear or anti-friction performances.

1. A grease composition comprising:

(A) a synthetic base oil in majority consisting of alkylaromatic(s);

(B) a thickener in majority consisting of at least one metal soap of fatty acids; and

(C) a solid lubricant in majority consisting of nanoparticulate polytetrafluoroethylene, at least 85% of the particles of which have a size of less than one micron.

2. The composition according to the preceding claim, wherein the oil in the form of alkylaromatics makes up at least 80% by weight of the base oil in said composition.

3. The composition according to claim 1, wherein the metal soap(s) make(s) up at least 80% by weight of the thickener in said composition.

4. The composition according to claim 1, wherein the solid lubricant consists of at least 80%, by weight of nanoparticulate polytetrafluoroethylene.

5. The composition according to claim 1, wherein the solid lubricant only consists of nanoparticulate polytetrafluoroethylene.

6. The composition according to claim 1, wherein the thickener is free of urea compounds.

7. The composition according to claim 1, wherein the composition is free of calcium carbonate.

8. The composition according to claim 1, wherein the composition comprises 0.1 to 10% by weight of solid lubricant in the form of nanoparticulate polytetrafluoroethylene.

9. The composition according to claim 1, wherein the polytetrafluoroethylene particles have an average size comprised between 150 and 800 nm.

10. The composition according to claim 1, wherein the synthetic base oils are selected from oils of the alkybenzene or alkylnaphthalene type.

11. The composition according to claim 1, wherein the synthetic base oil comprises at least one other mineral, synthetic or natural base oil.

12. The composition according to claim 1, wherein the soaps are simple metal soaps of either saturated or not, either hydroxylated or not, fatty acids comprising from 14 to 28 carbon atoms, or complex metal soaps of one or more either saturated or not, either hydroxylated or not fatty acids comprising from 14 to 28 carbon atoms, in a combination with one or more carboxylic acids with a short hydrocarbon chain comprising from 6 to 12 carbon atoms.

13. The composition according to claim 1, wherein the metal soaps of fatty acids are selected from titanium, aluminium, alkaline and earth alkaline metal soaps, preferably lithium, calcium, sodium, barium soaps.

14. The composition according to claim 1, wherein the composition comprises one or more anti-wear and/or extreme pressure agents.

15. The grease composition according to claim 1, wherein the composition comprises, based on the total weight of the composition:

from 50 to 90% by weight of the synthetic base oil;

from 1 to 15% by weight of the thickener in majority consisting of at least one metal soap of fatty acids;

from 0.1 to 10% by weight of solid lubricant in the form of nanoparticulate polytetrafluoroethylene powder with at least 85% of the particles which have a size of less than one micron; and

from 0 to 10% of one or more anti-wear and/or extreme pressure additives.

16. The composition according to the preceding claim, wherein the composition comprises 5 to 15% by weight based on the total weight of the composition, of a synthetic oil of the polyalphaolefin type.

17. The composition according to claim 1, wherein the composition comprises a base oil having a kinematic viscosity at 40° C., measured according to the ASTM D 445 standard, comprised between 10 and 120 mm^2/s.

18. The composition according to claim 1, wherein the composition has a consistency according to the ASTM D217 standard of more than 265 tenths of millimeters, and in that it has a consistency according to the ASTM D217 standard of more than 400 tenths of millimeters.

19. A method for preparing a grease, the method comprising:

dissolving one or more fatty acids in a fraction of the base oil or of the base oil mixture

adding metal compounds;

saponifying fatty acids with said metal compounds; and

incorporating nanoparticulate polytetrafluoroethylene, for which at least 85% of the particles have a size of less than one micron.

20. The composition according to claim 1, wherein the grease is adapted for use in automobile transmissions.

21. The composition according to claim 1, wherein the grease is adapted for use in at least one automobile member selected from: lubricated rolling bearings, machine tool slide rails or centralized greasing systems.

22. The composition according to claim 1, wherein the solid lubricant consists of at least 90% by weight of nanoparticulate polytetrafluoroethylene.

23. The composition according to claim 1, wherein it comprises 2 to 7% by weight of solid lubricant in the form of nanoparticulate polytetrafluoroethylene.

24. The composition according to claim 1, wherein the composition has a consistency according to the ASTM D217 standard comprised between 265 and 475 tenths of millimeters, and has a consistency according to the ASTM D217 standard comprised between 400 and 475 tenths of millimeters.

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