Grease composition

The present invention describes a grease composition comprising a base oil component, at least one thickener and at least one metal salt, wherein the grease composition comprises at least one metal salt of an organic acid and at least one metal salt of an inorganic acid and from 0.00005 wt% to 0.01 wt%, preferably from 0.0001 wt% to 0.005wt%, most preferably from 0.0001 wt% to 0.003wt% abrasive particles.
The present invention relates to a grease composition. Furthermore, the present invention relates to a method for producing the grease composition.

BACKGROUND OF THE INVENTION

Lubricants in roller bearings and friction bearings ensure that a film of lubricant, which transfers loads and separates different parts is established between parts that rub or slide against one another. This achieves the result that metallic surfaces do not come in contact with one another and therefore there is no wear. The lubricants must therefore meet high demands. These includes extreme operating conditions such as very high or very low rotational speeds, high temperatures caused by high rotational speeds or by long-distance heating, very low temperatures, e.g., in bearings that operate in a cold environment or which occur with use in aviation and space travel. Likewise, modern lubricants should be suitable for use under so-called clean room conditions in order to avoid soiling of the room due to abrasion and/or the consumption of lubricants. Furthermore, in use in modern lubricants, evaporation and thus "lackification," i.e., such that they become solidified after a short application and no longer manifests a lubricating effect, should be avoided. Especially high demands are also made of lubricants during use such that the running surfaces of the bearings are not attacked due to slight friction, so that the bearing surfaces run noiselessly and long running times without relubrication are promoted. Lubricants must also withstand the action of forces such as centrifugal force, gravitational force and vibrations.

In the past fifty years metal-coating compositions were developed especially for exploitation in harsh environments featuring high temperatures and pressures. Metal-coating lubricants are materials that form a non-oxidising thin metal film, such as a few micrometers thick copper film on the friction surfaces also on those surfaces not containing the film-forming metals. The protective thin metal film provides significant reduction of the friction coefficient even in marginal lubrication conditions and when friction surfaces are under high pressure.

Russian patents RU 2311447 and RU 2338777 disclose a metal-containing oil-soluble composition for lubricant greases. Said composition comprises metal salt of inorganic acid, metal salt of organic acid, aliphatic alcohol, aromatic amine, epoxy resin, succinimide polymer and 2-imine-substituted derivative of indoline. A known disadvantage of said composition is ineffective formation of the protective thin metal film on friction surfaces, thus making such a lubricant useless in applications where it is crucial to achieve a maximum degree of protection as soon as possible.

PURPOSE OF THE INVENTION

The purpose of the present invention is to eliminate the drawbacks mentioned above. The purpose of the present invention is to prolong the lifespan of moving parts such as parts of bearings, machines and vehicles by reducing temperatures of friction surfaces and improving abrasive resistance, thus reducing wear of their moving parts. This is achieved by protecting friction surfaces with a novel grease composition providing a fast formation of the protective thin metal film on friction surfaces.

A further purpose of the grease composition according to the present invention is to provide an environmentally friendly lubricant comprising significantly less toxic and environmentally harmful chemicals or components than the lubricants and lubricant additives currently available on the market. Furthermore, it was thus an object of the present invention to provide a grease composition which leads to a reduction in the fuel consumption. Furthermore, the grease composition should enable a longer grease change intervals and improved operational lifetime.

A further objective of the present invention is development of a lubricant for application on the railway transport that can sustain high unit loads; provide long-lasting operation life of conjugated pairs protecting them from contact fatigue damages, decreasing the wear of the friction pairs wheel-rail and traction units of traction vehicles, providing protection of the friction surfaces from hydrogen wear and implementing the auto-compensation of wear and damages. Especially with regard to the railroad application, the present grease composition should enable a higher blocking efficiency regarding lubricant losses to the road bed.

An additional technical task of the present invention is development of a lubricant that can provide long-lasting
operation time of roller bearings of axle boxes with a low friction coefficient and eliminate overheating of roller bearings in long-term operation as well as reduce damages through hydrogen wear.

These improvements should be achieved without environmental drawbacks.

SUMMARY OF THE INVENTION

These objects and further objects which are not stated explicitly but are immediately derivable or discernible from the connections discussed by way of introduction herein are achieved by the grease composition being characterized by what is disclosed in claim 1. Appropriate modifications to the inventive greases are protected in the subclaims which refer back to claim 1. The method for producing a grease composition according to the present invention is characterized by what is disclosed in claim 13. The bearing according to the present invention is characterized by what is disclosed in claim 14. The chassis according to the present invention is characterized by what is disclosed in claim 15. The present invention provides a grease composition comprising a base oil component, at least one thickener and at least one metal salt, wherein the grease composition comprises at least one metal salt of an organic acid and at least one metal salt of an inorganic acid and from 0.00005 wt% to 0.01 wt%, preferably from 0.0001 wt% to 0.005 wt%, most preferably from 0.0001 wt% to 0.003 wt% abrasive particles.

Preferably, the average diameter size of abrasive particles ranges from 0.5 μm to 20 μm, preferably from 1 μm to 10 μm, most preferably from 1 μm to 3 μm. Preferably, the abrasive particles have a hardness of at least 7 on the Mohs scale. Preferably, the abrasive particles comprise carbonates, nitrates, carbides and/or oxides of elements of boron, carbon and/or alkaline earth metal groups.

Preferably, the abrasive particles comprise carbonates, nitrides, carbides and/or oxides of elements of boron, carbon and/or alkaline earth metal groups.

Preferably, the grease composition comprises a NLGI consistency number according to DIN 51818 from 0 to 6, preferably from 0 to 6 and more preferably from 1 to 5.

Preferably, the grease composition comprises a thickener on the basis of soap, a thickener on the basis of a polymer and/or an inorganic thickener.

Preferably, the grease composition comprises particles having a size of less than 0.1 micron.

Preferably, the grease composition comprises a drop point of at least 180°C according to DIN ISO 2176.

Furthermore, the present invention provides a method for producing a grease composition in accordance with the definitions provided above and below comprising mixing a base oil with at least one metal salt of an inorganic acid and at least one metal salt of an inorganic acid and from 0.00005 wt% to 0.01 wt%, preferably from 0.0001 wt% to 0.005 wt%, most preferably from 0.0001 wt% to 0.003 wt% abrasive particles and a thickener.

In addition thereto, the present invention provides a bearing, preferably a wheel bearing or a roller bearing, comprising a grease composition in accordance with the definitions provided above and below. Moreover, the present invention provides a chassis comprising a grease composition in accordance with the definitions provided above and below.

Furthermore, the present invention provides a grease composition which leads to a reduction in the fuel consumption. Preferably, the grease composition according to the present invention does not comprise essential amounts of phosphorus- nor sulfur-based compounds.

Moreover, the grease composition enables a longer grease change intervals and improved operational lifetime. In addition thereto, the present grease composition enables a higher blocking efficiency regarding lubricant losses to the road bed.

DETAILED DESCRIPTION OF THE INVENTION

The invention is based on research work, the aim of which was to show that a certain concentration of abrasive particles accelerate formation of the protective thin metal film. According to the studies, abrasive particles enhance diffusion of metal ions, which are present in lubricant in the form of metal salts, into the crystal lattice of friction surfaces.

The present invention is focused on a grease composition. Here, a grease composition means a substance introduced between moving surfaces to reduce the friction between them, i.e. a grease composition is any kind of a natural or a synthetic lubricating substance having a semisolid or plastic consistency. The compounds of the grease composition of the present invention react on friction surfaces and form a non-oxidising thin metal film on said surfaces, thus reducing mechanical wear and tear of the surfaces the grease composition has been applied on. Therefore, the grease composition can be classified as a metal-coating composition.

The grease composition of the present invention comprises a base oil component, at least one thickener and...
at least one metal salt.

[0030] Base oils that are useful in the practice of the present invention may be selected from natural oils, synthetic oils and mixtures thereof.

[0031] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrogenated, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0032] Synthetic lubricating oils include hydrocarbon oils and halogen-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutyl, polypentenyl, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivatives, analogs and homologs thereof.

[0033] Preferred base oils include those obtained by producing heavy linear chain paraffins in the Fischer-Tropsch process where hydrogen and carbon monoxide obtained by the gasification process (partial oxidation) of natural gas (methane etc.) are used and then subjecting this material to a catalytic cracking and isomerisation process.


[0035] Alkylene oxide polymers and interpolymer derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or thereabout); polyalkylalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C3-C8 fatty acid esters and C13-Ox acid diester of tetraethylene glycol.

[0036] Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Examples of such esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, diocyl sebacate, diisooctyl azelate, disodocetyl azelate, diocyt phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0037] Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and triplentaerythritol.

[0038] Silicon-based oils such as the polyalkyl-, polycarbonyl- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetrakispropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl) disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes.

[0039] The oil of lubricating viscosity useful in the practice of the present invention may comprise one or more of a Group I, Group II, Group III, Group IV or Group V oil or blends of the aforementioned oils. Definitions for the oils as used herein are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes oils as follows:

a) Group I oils contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.

b) Group II oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1. Although not a separate Group recognized by the API, Group II oils having a viscosity index greater than about 110 are often referred to as "Group II+" oils.

c) Group III oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 1.

d) Group IV oils are polyalphaolefins (PAO).

e) Group V oils are all other base stocks not included in Group I, II, III, or IV.
Preferably the volatility of the base oil, as measured by the Noack test (ASTM D5880), is less than or equal to about 40%, such as less than or equal to about 35%, preferably less than or equal to about 32%, such as less than or equal to about 28%, more preferably less than or equal to about 16%. Preferably, the viscosity index (VI) of the base oil is at least 100, preferably at least 110, more preferably greater than 120.

Base oils, also referred to as oils of lubricating viscosity useful in the context of the present invention may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy duty diesel oils. Generally, the viscosity of the oil ranges from about 2 mm²s⁻¹ (centistokes) to about 200 mm²s⁻¹, especially from about 4 mm²s⁻¹ to about 40 mm²s⁻¹ as measured at 100 °C.

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 mm²s⁻¹ (centistokes), preferentially between 10 and 50 mm²s⁻¹ (centistokes), preferably between 20 and 40 mm²s⁻¹ (centistokes), 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 mm²s⁻¹ (centistokes), preferentially between 30 and 40 mm²s⁻¹ (centistokes), preferably between 35 and 37 mm²s⁻¹ (centistokes), so as to guarantee an adequate oil film under higher loads.

In addition to the base oil, the present grease composition comprises a thickener. These thickeners include thickeners on the basis of soap, thickeners on the basis of a polymer and/or inorganic thickeners.


The greases according to the invention are preferably thickened with soaps, preferably 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.

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).

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.

The saponification agent used for making the soap may be a metal compound of lithium, sodium, calcium, barium, titanium, aluminum, 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.

Preferably a lithium complex thickener can be used in the present grease composition. For example, the lithium complex thickener can comprise a lithium soap derived from a fatty acid containing an epoxy group and/or ethylenic unsaturation and a dilithium salt derived from a straight chain dicarboxylic acid and/or, in one embodiment, a lithium salt derived from a hydroxy-substituted carboxylic acid such as salicylic acid.

According to a preferred embodiment of the present invention, the thickener can be a lithium soap or a lithium complex soap prepared from hydroxy fatty acid having from 12 to 24 carbon atoms.

Preferably, the thickener can be a complex of a lithium soap of a C₃₂ to C₃₄ hydroxy fatty acid and a monolithium salt of boric acid and can include a lithium salt of a second hydroxy carboxylic acid such as salicylic acid.

The complex can comprise a lithium soap of a C₁₈ to C₂₀ hydroxy fatty acid thickener antioxidant comprising an alkali metal salt of hydroxy benzoic acid and a diozime compound. The alkali metal salt of hydroxy benzoic acid

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
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<tbody>
<tr>
<td>Saturates</td>
<td>ASTM D2007</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>ASTM D2270</td>
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<tr>
<td>Sulfur</td>
<td>ASTM D4294</td>
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include dilithium salicylate.

The complex can be a lithium soap which is a combination of a dilithium salt of a C₄ to C₁₂ dicarboxylic acid, e.g., dilithium azelate, a lithium soap of a 9-, 10- or 12-hydroxy C₁₂ to C₂₄ fatty acid, e.g., lithium 12-hydroxy stearate; and a lithium salt formed in-situ in the grease from a second hydroxy carboxylic acid wherein the -OH group is attached to a carbon atom not more than 6 carbons removed from the carboxyl group and wherein either of those groups may be attached to either aliphatic or aromatic portions of the materials.

Or, the lithium complex can comprise a combination of a complex lithium soap thickener, a lithium salt of a C₅ to C₁₄ hydroxy carboxylic acid and a thiadiazole. The grease may also optionally and preferably contain additional antioxidants, preferably amine type or phenol type anti-oxidants, most preferably amine type antioxidants.

In one embodiment, the lithium complex thickener is simply a lithium salt of a carboxylic acid, such as stearic acid and oleic acid, and in particular a hydroxy carboxylic acid, such as hydroxystearic acid. Such a thickener can be prepared, for example, by reacting lithium hydroxyl monohydrate with the hydroxystearic acid, stearic acid and/or oleic acid.

According to a preferred embodiment the thickener preferably include a lithium soap of 12-oxystearic acid and a lithium soap of oleic acid. More preferably, the weight ratio of the lithium soap of 12-oxystearic acid to the lithium soap of oleic is in the range of 10:1 to 1:2, more preferably 5:1 to 1:1 and most preferably 4:1 to 2:1.

Thickeners based on polymers include polycarbamides (polyureas) and polytetrafluoroethylene. Thickeners based on urea compounds are disclosed in WO 2011/020863 A1. Furthermore, greases comprising polymeric thickeners are disclosed in WO 2012/076025 A1. The documents WO 2011/020863 A1 and WO 2012/076025 A1 are expressly incorporated herein by reference for their disclosure regarding thickeners based on polymers.

Furthermore, inorganic thickeners can be applied such as bentonite, amorphous hydrophilic silicon oxide particles and silica gel. Preferably silica particles having a mean particle size in the range of 5 to 50 nm can be used as described in US 2012/149613 A1. The document US 2012/149613 A1 is expressly incorporated herein by reference for its disclosure regarding silica particles useful as thickeners.

The thickener mentioned above can be used as a single compound or as a mixture of different compounds being classified in the same class or as mixtures of thickeners being classified in different classes.

Regarding the choice of thickener, thickeners being based on soaps are preferred over thickeners based on polymers or inorganic thickeners.

The weight ratio of base oil to thickener in the grease composition is known per se and is described in the literature mentioned above and below. In general, this ratio depends on the NLGI consistency number according to DIN 51818 and is in the range from 100:1 to 100:30, preferably 100:2 to 100:25, in particular 100:5 to 100:15.

For example, metal soaps are preferably used at contents of the order of 1 to 60% by weight, preferentially from 2 to 50% or further from 4 to 40% or from 4.5 to 30% 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%, preferably 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%, preferably 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. 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.

According to a special aspect of the present invention, the grease composition may preferably comprise about 8-12 weight percent (wt. %) lithium soap of 12-oxystearic acid and 1,5-3,0 wt. % lithium soap of oleic acid 1,5-3,0.

Higher amounts of thickeners or the use of further additives will lead to greases having a higher grade according to the NLGI classification, such as grade 3, grade 4, grade 5 or grade 6. For example, the thickening activity of some thickeners can be increase by using of copolymer as an additive. These copolymers are commonly used as viscosity index improvers and are described below. The copolymer can be a hydrocarbon based copolymer such as a copolymer of styrene and butadiene or ethylene and propylene. In one embodiment, the copolymer additive is a copolymer of styrene and butadiene. It has been found that use of a small amount of such a copolymer, e.g. from 2-6 weight percent, or from 2-5 weight percent, or in another embodiment, from 3-4 weight percent, in combination with a lithium complex thickener, results in a 25-50% increase in thickener yield.

Preferably, the greases will comprise a major amount, e.g., greater than 50% by weight of the base oil, and a minor amount of the thickener and any other additives, i.e., less than 50% by weight. The greases of the present invention may, of course, contain any of the other, typical grease additives such as rust inhibitors, barium dinonyl naphthalene sulfonate, order modifiers, tackiness agents, extreme pressure agents, water shedding agents, dyes, etc. Typical additives and their function are described in Modern Lubricating Greases by C. J. Boner, Scientific Publication (G.B.) Ltd. 1976.

In addition to the base oil and the thickener, a grease composition of the present invention includes at least one metal salt.
As well known for those skilled in the art, in order to form a metal film on the metal friction surfaces, the grease shall comprise metal ions. In addition, said ions must have higher ionization energy that that of the surface metal ions; i.e. if a friction surface is made of steel, the grease must comprise ions of metals having higher ionization energy than Fe. In that case, metal ions present in the lubricant fulfill the vacancies and diffuse inside the frictional surface removing dislocations caused by friction and forming crystals of protective thin metal film on the surface.

Addition of oil soluble metal salts of inorganic and organic acids to grease is crucial for formation of a protective thin metal film on friction surfaces where grease was applied. Said metal salts provide metal ions which fulfill the open vacancies and diffuse inside the frictional surface forming a thin metal film. This is a known practise in the art, with a composition disclosed in RU2277579, RU2311447, RU2338777 and WO 2012/076025 A1 being examples. The documents RU2277579, RU2311447, RU2338777 and WO 2012/076025 A1 are expressly incorporated herein by reference for their disclosure regarding metal salts. Furthermore, an additive comprising metal salts useful for the present invention is commercially available under the trademark VALENA®. However, as an essential difference from the prior art, the lubricant composition according to the present invention comprises abrasive particles which enhance diffusion of metal ions, present in the composition in the form of metal salts, into friction surfaces and thus accelerate formation of protective metal film.

The grease composition according to the present invention comprises oil soluble metal salts of inorganic and organic acids and further comprises from 0.00005 wt% to 0.01 wt%, preferably from 0.0001 wt% to 0.005 wt%, most preferably from 0.0001 wt% to 0.003 wt% abrasive particles.

When added to friction surfaces, the grease composition according to the present invention forms a protective layer at the friction surfaces through physical bonding between the metal ions of the salt and the friction surfaces. The abrasive particles enhance diffusion of metal ions into friction surfaces and thus accelerate formation of protective metal film, as they remove oxide films from the friction surfaces. In other words abrasive particles, by removing oxidized films from the friction surface, they catalyse the build-up of the protective metal film through physical bonding between the metal ions of the salts and the friction surfaces. Oxide films, which typically form on metal surfaces due to air exposure, make the metal more resistant to chemical reactions. With no oxide films on the surfaces the protective metal film forms faster. In addition thereto, the prevention of oxide films improves the wear resistance and lowers the scuffing of the metal surface.

By abrasive particles it is meant here either naturally occurring or fabricated granular material composed of finely divided hard particles, such as mineral or metal particles. These particles are useful for removing oxide films from the friction surfaces and, hence should have an appropriate hardness. It shall be noted that the exact chemical composition of abrasive particles is of secondary importance; however, the crucial matter is the concentration of abrasive particles in an composition. According to the extensive studies, the optimal concentration of abrasive particles in the composition varies from about 0.00005 wt% to about 0.01 wt%, where wt% is mass percentage. The optimal concentration depends on factors such as the composition of the lubricant and the additives, the size of abrasive particles, etc. Studies show that when the composition comprises from about 0.0001 wt% to about 0.005 wt% of abrasive particles, the protective metal film forms within about 30 seconds from the start of the friction between the lubricated surfaces (i.e. from the moment the lubricated engine or motor starts running). Measurements preformed for similar lubricant compositions without abrasive particles indicate that in these cases the protective metal film forms in about five minutes, which is a considerably longer period.

In another preferred embodiment of the present invention the average diameter size of abrasive particles ranges from 0.5 μm to 20 μm, preferably from 1 μm to 10 μm, most preferably from 1 μm to 3 μm. The exact chemical composition of abrasive particles may vary, however the average diameter size of the abrasive particles ranges approximately from 0.5 μm to 20 μm, preferably from 1 μm to 10 μm, most preferably from 1 μm to 3 μm. This means that statistically the majority of the abrasive particles has said diameter, however, variations around these values are possible. Therefore, in a grease composition one can find the majority of the abrasive particles having a diameter of about 1 μm; however, the same grease composition may as well comprise abrasive particles having a diameter of about 5 μm or 20 μm. Similarly, the majority of abrasive particles found in another grease composition may have a diameter of about 10 μm; however, the same grease composition may also comprise abrasive particles having a diameter of about 3 μm. Studies show that abrasive particles having a diameter from 0.5 μm to 20 μm remove oxide films from the friction surfaces most efficiently and thus accelerate protective film formation.

In another preferred embodiment of the present invention abrasive particles have a hardness of at least 6, more preferably at least 6.5 and especially preferably of at least 7 on the Mohs scale. Therefore, abrasive particles comprise finely divided particles of ceramic materials, minerals, metals and/ or other compounds having a hardness of at least 6, more preferably at least 6.5 and especially preferably of at least 7 or more on the Mohs scale. Amongst others, the following minerals have a hardness of at least 7 on the Mohs scale, thus being suitable for use as abrasive particles: quartz, garnet, beryl, chrysoberyl, topaz, emerald, spinel, corundum, boron and diamond. In addition, at least the following metals have a hardness of at least 6 on the Mohs scale, thus also being suitable for use as abrasive particles: osmium, steel, tungsten, chromium and titanium with osmium, tungsten, chromium and titanium having a hardness of at least 7.
on the Mohs scale. Further, at least the following ceramic materials having a hardness of at least 7 on the Mohs scale can be used as abrasive particles: silicon carbide, tungsten carbide, titanium carbide, rhenium diboride and titanium diboride. According to the preferred embodiment of the present invention, abrasive particles comprise any of the above mentioned ceramic materials, minerals or metals, or mixtures thereof, in a form of a fine powder or a granular mixture.

In another preferred embodiment of the present invention abrasive particles comprise carbonates, nitrides, carbides and/or oxides of elements of boron, carbon and/or alkaline earth metal groups. Here, the boron group is a periodic table group consisting of boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl), and ununtrium (Uut); the carbon group is a periodic table group consisting of carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb), and ununquadium (Uuuq); and alkaline earth metals consist of beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). Examples of compounds fulfilling the above conditions are, amongst others, silicon dioxide, boron carbide, boron nitride and aluminium dioxide. According to the preferred embodiment of the present invention, abrasive particles comprise any of the above compounds separately, or a mixture thereof, in a form of a fine powder or a granular mixture.

According to the present invention the oil soluble metal salts of inorganic acid comprise oil soluble metal salts, i.e. chlorides, bromides and/or iodides of at least one of the following metals: Cu, Co, Pb, Sn, Ni. More preferably, the oil soluble metal salts of inorganic acid comprise CuCl, CuBr, CuJ, CuCl₂, CuBr₂, CoCl₂, CoBr₂, CoJ₂, PbCl₂, PbBr₂, PbJ₂, SnCl₂, SnBr₂, SnJ₂, NiCl₂, NiBr₂ and/or NiJ₂. Copper salts are especially preferred.

Further, according to the present invention the oil soluble metal salts of organic acid comprises acids comprising carbon atoms and oxygen atoms. Regarding the organic acid salts, copper salts are especially preferred.

The organic metal salt, preferably the organic copper salt may be blended into the oil as any suitable oil soluble metal compound, preferably copper compound. By oil soluble we mean the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The organic metal salt, preferably the organic copper salt may be added as the metal salt, preferably copper salt of a synthetic or natural carboxylic acid. Examples include C₁₅ to C₁₈ fatty acids such as stearic or palmitic, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500 or synthetic carboxylic acids are preferred because of the improved handling and solubility properties of the resulting metal carboxylates, preferably copper carboxylates.

Exemplary of useful copper compounds are copper (Cu¹ and/or CuII) salts of alkenyl succinic acids or anhydrides. The salts themselves may be neutral, basic or acidic.

Examples of the metal salts of this invention are Cu salts of polyisobutenyl succinic anhydride (hereinafter referred to as Cu-PIBSA), and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g., Cu²⁺. The preferred substrates are polyalkenyl succinic acids in which the alkyl group has a number average molecular weight (Mn) greater than 700. The alkyl group desirably has a Mn from 900 to 1400, and up to 2500, with a Mn of about 950 being most preferred. Especially preferred is polyisobutylene succinic acid (PIBSA). These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between 70°C and 200°C. Temperatures of 110°C to 140°C are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about 140°C for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

Preferred metal salts of organic acids comprising organic acids having from 15 to 18 carbon atoms in their molecular formula, such as metal salts of oleic acid CH₃(CH₂)₇CH=CH(CH₂)₇COOH. Preferred examples of a metal salt of organic acids are tin oleate C₃₅H₆₆O₄Sn, copper oleate C₃₆H₆₆O₄Cu, nickel oleate C₃₆H₆₆O₄Ni, lead oleate C₃₆H₆₆O₄Pb and cobalt oleate C₃₆H₆₆O₄Co with copper oleate C₃₆H₆₆O₄Cu being especially preferred. It shall be noted that said oil soluble metal salts of inorganic and organic acids are completely dissolved in the end product, i.e. in a grease composition according to the present invention.

In another preferred embodiment of the present invention the composition comprises, in addition to abrasive particles and oil soluble metal salts of inorganic and organic acids, at least one of the following: an aliphatic alcohol, a succinimide derivative, an aromatic amine, an epoxy resin and/or a 2-iminosubstituted indoline.

In another preferred embodiment of the present invention the succinimide derivative comprises S-5A polyalkenyl succinimide, the aromatic amine comprises homotype diphenylamine and the epoxy resin comprises commercially available aliphatic epoxy resin ¹ ¹ ДЭГ-1, produced by condensation of epichlorohydrin with glycol.


improvers. [0085] Preferred viscosity index improvers for grease compositions advantageously increase the viscosity of the lubricating oil being released by the grease composition at higher temperatures when used in relatively small amounts (have a high thickening efficiency (TE)), provide reduced lubricating oil resistance at low temperatures and be resistant to mechanical degradation and reduction in molecular weight in use (have a low shear stability index (SSI)).

[0086] Viscosity index (VI) improvers include polymers based on olefins, such as polyisobutylene, copolymers of ethylene and propylene (OCP) and other hydrogenated isoprene/butadiene copolymers, as well as the partially hydrogenated homopolymers of butadiene and isoprene and star copolymers and hydrogenated isoprene star polymers, polyalkyl (meth)acrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, interpolymer of styrene and acrylic esters, and hydrogenated copolymers of styrene/isoprene and styrene/butadiene. The molecular weight of polymers useful as viscosity index improver in accordance with the present invention can vary over a wide range since polymers having number-average molecular weights (Mn) as low as about 2,000 can affect the viscosity properties of an oleaginous composition. The preferred minimum Mn is about 10,000; the most preferred minimum is about 20,000. The maximum Mn can be as high as about 12,000,000; the preferred maximum is about 1,000,000; the most preferred maximum is about 750,000. An especially preferred range of number-average molecular weight for polymer useful as viscosity index improver in the present invention is from about 15,000 to about 500,000; preferably from about 20,000 to about 250,000; more preferably from about 25,000 to about 150,000. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by size exclusion chromatography (also known as gel permeation chromatography (GPC)) which additionally provides molecular weight distribution information, see W. W. Yau, J.J. Kirkland and D.D. Bly, “Modern Size Exclusion Liquid Chromatography”, John Wiley and Sons, New York, 1979.

[0087] The polydispersity index (Mw/Mn) of preferred polymers useful as viscosity index improver in accordance with the present invention is less than about 10, preferably less than about 5, more preferably less than about 4 and most preferably less than about 3 e.g., from 1.05 to 3.5, most preferably from 1.1 to 3. Mw is the weight average molecular weight of the polymer as measured by Gel Permeation Chromatography (GPC) with a polystyrene standard.

[0088] “Thickening Efficiency” (TE) is representative of a polymers ability to thicken oil per unit mass and is defined as:

$$TE = \frac{2}{c ln2} \ln \left( \frac{k_{\text{oil}} + \text{polymer}}{k_{\text{oil}}} \right)$$

wherein c is polymer concentration (grams of polymer/100 grams solution), $k_{\text{oil}} + \text{polymer}$ is kinematic viscosity of the polymer in the reference oil, and $k_{\text{oil}}$ is kinematic viscosity of the reference oil. The TE is preferably measured at 100 °C.

[0089] The viscosity index improver useful for the present invention preferably has a TE of from about 1.5 to about 4.0, preferably from about 1.6 to about 3.3, more preferably from about 1.7 to about 3.0.

[0090] “Shear Stability Index” (SSI) measures the ability of polymers used as V.I. improvers in crankcase lubricants to maintain thickening power during use and is indicative of the resistance of a polymer to degradation under service conditions. The higher the SSI, the less stable the polymer, i.e., the more susceptible it is to degradation. SSI is defined as the percentage of polymer-derived viscosity loss and is calculated as follows:

$$SSI = 100 \times \frac{k_{\text{fresh}} - k_{\text{after}}}{k_{\text{fresh}} - k_{\text{oil}}}$$

wherein $k_{\text{oil}}$ is the kinematic viscosity of the base oil, $k_{\text{fresh}}$ is the kinematic viscosity of the polymer-containing solution before degradation and $k_{\text{after}}$ is the kinematic viscosity of the polymer-containing solution after degradation. SSI is conventionally determined using ASTM D6278-98 (known as the Kurt-Orban (KO) or DIN bench test). The polymer under test is dissolved in suitable base oil (for example, solvent extracted 150 neutral) to a relative viscosity of 9 to 15 mm²s⁻¹ (centistokes) at 100 °C and the resulting fluid is pumped through the testing apparatus specified in the ASTM D6278-98 protocol for 30 cycles. As noted above, a 90 cycle shear stability test (ASTM D7109) was approved in 2004.

[0091] The shear stability index (SSI, 30 cycles) according to ASTM D6278-98 of preferred polymers useful as viscosity index improver in accordance with the present invention is preferably less than about 60 %, more preferably less than about 50 %, more preferably less than about 40 %. Preferred ranges are e.g. from about 1 % to about 60 %, preferably from about 2 % to about 50 %, more preferably from about 5 % to about 40 %.

[0092] Polymers based on olefins include monomers consisting of carbon atoms and hydrogen atoms, such as ethylene, propylene, butylene and diene monomers, such as butadiene. Preferably, the polymers based on olefins comprise at
least 30 wt%, more preferably at least 50 wt% and most preferably at least 80 wt% repeating units being derived from olefin monomers. Preferred olefin copolymers (or OCP) useful as viscosity index improvers conventionally comprise copolymers of ethylene, propylene and, optionally, a diene. Small polymeric side chains do not exert a substantial viscosity modifying effect in oil. Polymerized propylene has one methyl branch for every two backbone carbon atoms. Ethylene polymer is substantially straight chained. Therefore, at a constant amount of polymer in oil (treat rate), an OCP having a higher ethylene content will display an increased high temperature thickening effect (thickening efficiency, or TE). However, polymer chains having long ethylene sequences have a more crystalline polymer structure.

[0093] Due to their molecular architecture, star polymers are known to provide improved shear stability compared to OCPs. VI improvers that are star polymers made by hydrogenation of anionically polymerized isoprene are commercially available. Anionic polymerization results in a relatively low molecular weight distribution (Mw/Mn). Hydrogenation results in alternating ethylene/propylene units having a composition comparable to a polymer derived from 40 wt.% ethylene and 60 wt.% propylene. These VI improvers provide excellent shear stability, good solubility and excellent cold temperature properties.


[0095] Polyalkyl (meth)acrylates are based on alkyl (meth)acrylate monomers conventionally comprising 1 to 4000 carbon atoms in the alkyl group of the (meth)acrylates. Preferably, the polyalkyl (meth)acrylates are copolymers of alkyl (meth)acrylate monomers having 1 to 4 carbon atoms in the alkyl group, such as methyl methacrylate, ethyl methacrylate and propyl methacrylate and alkyl (meth)acrylate monomers having 8 to 4000 carbon atoms, preferably 10 to 400 carbon atoms and more preferably 12 to 30 carbon atoms in the alkyl group. Preferred polyalkyl (meth)acrylates are described in the patents US 5,130,359 and US 6,746,993. The documents US 5,130,359 and US 6,746,993 are expressly incorporated herein by reference for their disclosure regarding viscosity index improvers based on polyalkyl (meth)acrylates.

[0096] Preferably, the viscosity index improver may comprise dispersing groups. Dispersing groups including nitrogen-containing and/or oxygen-containing functional groups are well known in the art. Regarding functional groups nitrogen-containing groups are preferred. One trend in the industry has been to use such “multifunctional” VI improvers in lubricants to replace some or all of the dispersant. Nitrogen-containing functional groups can be added to a polymeric VI improver by grafting a nitrogen- or hydroxy- containing moiety, preferably a nitrogen-containing moiety, onto the polymeric backbone of the VI improver (functionalizing). Processes for the grafting of a nitrogen-containing moiety onto a polymer are well known in the art and include, for example, contacting the polymer and nitrogen-containing moiety in the presence of a free radical initiator, either neat, or in the presence of a solvent. The free radical initiator may be generated by shearing (as in an extruder) or heating a free radical initiator precursor, such as hydrogen peroxide. In the context of polyalkyl (meth)acrylate polymers, polymers having functional groups, preferably nitrogen-containing functional groups can be achieved by using comonomers comprising nitrogen-containing groups such as dimethylaminoethyl methacrylate (U.S. Pat. No. 2,737,496 to E. I. Dupont de Nemours and Co.), dimethylaminomethylmethacrylamide (U.S. Pat. No. 4,021,357 to Texaco Inc.) or hydroxyethyl methacrylate (U.S. Pat. No. 3,249,545 to Shell Oil Co).


[0098] The amount of nitrogen-containing monomer will depend, to some extent, on the nature of the substrate polymer and the level of dispersancy required of the polymer. To impart dispersancy characteristics to copolymers, the amount of nitrogen-containing and/or oxygen-containing monomer is suitably between about 0.4 and about 10 wt. %, preferably from about 0.5 to about 5 wt. %, most preferably from about 0.6 to about 2.2 wt. %, based on the total weight of polymer.


[0100] The viscosity index improvers may be used as a single polymer or as a mixture of different polymers, for example, a combination of a polymer based on an olefin, such as polyisobutylene, copolymers of ethylene and propylene (OCP) and other hydrogenated isoprene/butadiene copolymers, as well as the partially hydrogenated homopolymers of butadiene and isoprene and/or star copolymers and hydrogenated isoprene star polymers, preferably a copolymer of ethylene and propylene (OCP) with an VI improver comprising polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and/or hydrogenated
copolymers of styrene/isoprene and/or styrene/butadiene. Preferably a mixture of at least one polymer based on olefins, preferably copolymers of ethylene and propylene (OCP) and of at least one polyalkyl (meth)acrylate can be used.

The grease composition may preferably contain a VI improver useful for the invention in an amount of from about 0 wt. % to about 30 wt. %, preferably from about 0.3 wt. % to about 25 wt. %, more preferably from about 0.4 wt. % to about 15 wt. %, stated as mass percent active ingredient (Al) in the total lubricating oil composition.

The viscosity index improvers are widely generally sold in the market as commercial products. For example, there are commercial products of VISCOLPLEX® (by Evonik Rohmax GmbH) and ACRU°BE® (by Sanyo Chemical) as a poly(meth)acrylate reagent. Infineum® V534 and Infineum® V501 available from Infineum USA L.P. and Infineum UK Ltd. are examples of commercially available amorphous OCP. Other examples of commercially available amorphous OCP VI improvers include Lubrizol® 7065 and Lubrizol® 7075, available from The Lubrizol Corporation; Jilin® 0010, available from PetroChina Jilin Petrochemical Company; and NDR015, available from Dow Elastomers L.L.C. An example of a commercially available star polymer VI improver having an SSI equal to or less than 35 is Infineum® SV200, available from Infineum USA L.P. and Infineum UK Ltd. Other examples of commercially available star polymer VI improver having an SSI equal to or less than 35 include Infineum® SV250, and Infineum® SV270, also available from Infineum USA L.P. and Infineum UK Ltd.

Multifunctional viscosity index improvers are available from Evonik Rohmax GmbH under the trade designations "Acryloid 985", "Viscoplex 6-054", "Viscoplex 6-954" and "Viscoplex 6-565" and from The Lubrizol Corporation under the trade designation "LZ 7720C".

The present grease composition may comprise further additives with the provision that the content of sulfur or phosphorus should be as low as possible. These additives include friction modifiers, antioxidants demulsifiers, dispersants and pour point depressants.

As antioxidants, hindered phenols or amines, for example phenyl alpha naphthylamine are generally used. Demulsifiers which are generally applied are polyalkylene glycol ethers. Preferred friction modifiers are compounds based on poly(meth)acrylates as described in WO-A-2004/087850, WO 2006/105926, WO 2006/007934 and WO 2005/097956. The documents WO-A-2004/087850, WO 2006/105926, WO 2006/007934 and WO 2005/097956 are expressly incorporated herein by reference for their disclosure regarding poly(meth)acrylates useful as friction modifiers. Furthermore, polymers such as nanoparticulate polytetrafluoroethylene can be added as described e. g. in US 2011/306527 A1. The document US 2011/306527 A1 is expressly incorporated herein by reference regarding poly(meth)acrylates useful as friction modifiers.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing slide gloculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight alkyl succinimides, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetra-ethylene pentamine and borated salts thereof.

The ashless dispersants include the polyalkenyl or borated polyalkenyl succinimide where the alkenyl groups are derived from a C2-C4 olefin, especially polyisobutenyl having a number average molecular weight of 700 to 5,000. Other well-known dispersants include ethylene-propylene oligomers with N/O functionalities and oil soluble polyol esters of hydrocarbon substituted succinic anhydride, e. g., polyisobutenyl succinic anhydride, and the oil soluble oxazoline and lactone oxazoline dispersants derived from hydrocarbon substituted succinic anhydride and disubstituted amino alcohols. Lubricating oils preferably contain 0.5 to 5 wt. % of ashless dispersant.

The pour point improvers include especially polyalkyl (meth)acrylates (PAMA) having 1 to 30 carbon atoms in the alcohol group, C2 to C18 dialkyl fumarate/vinyl acetate copolymers and chlorinated paraffin-naphthalene condensation products. Lubricating oils preferably contain up to 5 wt. %, more preferably 0.01 to 1.5 wt. % of pour point improvers. These are widely generally sold in the market as commercial products. For example, there are commercial products of VISCOPEN® (by Evonik Rohmax GmbH), ACRU°BE® (by Sanyo Chemical) and PLEXOL® (by Nippon Acryl) as a poly(meth)acrylate reagent; and commercial products of LUBRAN® (by Toho Chemical) as a chlorinated paraffin-naphthalene condensation product. Preferred are poly(meth)acrylates.


Table 2 shows preferred compositions for lubricants according to the present invention.

<table>
<thead>
<tr>
<th>Amount in wt% preferred</th>
<th>Amount in wt% more preferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>base oil</td>
<td>50 to 98.0</td>
</tr>
<tr>
<td>thickener</td>
<td>0.1 to 60</td>
</tr>
</tbody>
</table>
The grease composition preferably comprises a NLGI consistency number according to DIN 51818 from 0 to 6, especially from 0 to 6 and more preferably from 1 to 5.

According to a special aspect of the present invention, the grease composition comprises a drop point of at least 180 °C, more preferably at least 190 °C according to DIN ISO 2176.

Preferred lubricating grease compositions are preferably suitable for applications for upper service temperatures of more than 120 °C up to 260 °C and for low service temperatures of -60 °C according to DIN 51285. They may also be used at upper service temperatures of more than 180 °C and for low service temperatures down to -60 °C according to DIN 51825.

Preferably, the grease composition comprises at most 0.2 wt%, especially at most 0.1 wt%, preferably at most 0.05 wt%, more preferably at most 0.03 wt%, and most preferably at most 0.01 wt% of sulfur. The amount of sulfur in the lubricant composition should be as low as possible in order to improve the environmental acceptability. The amount of sulfur can be determined according to ASTM D4294.

Preferably, the sulfur content of the grease composition is identical or smaller than the sulfur content of the base oil. No sulfur containing additives are needed or added.

Preferably, the grease composition comprises at most 0.05 wt%, especially at most 0.03 wt%, preferably at most 0.01 wt%, more preferably at most 0.003 wt%, and most preferably at most 0.001 wt% of phosphorus. The amount of phosphorus in the grease composition should be as low as possible in order to improve the environmental acceptability. The amount of phosphorus can be determined according to ASTM D1091.

Preferably, the phosphorus content of the grease composition is identical or smaller than the phosphorus content of the base oil. No phosphorus containing additives are needed or added.

According to a preferred aspect of the present invention the grease composition comprises at most 0.2 wt%, especially at most 0.1 wt%, preferably at most 0.05 wt%, more preferably at most 0.03 wt%, more preferably at most 0.02 wt%, and most preferably at most 0.01 wt% of sulfated ash. The amount of sulfated ash in the grease composition should be as low as possible in order to improve the environmental acceptability. The amount of sulfated ash can be determined according to ASTM D874.

Preferably, the sulfated ash of the grease composition is identical or smaller than the sulfated ash of the base oil.

The low amount of sulfur, phosphorus and sulfated ash in the grease composition can be obtained by using base oils having low sulfur and low phosphorus content and by omitting sulfur and phosphorus containing additives. It should be noted that prolongation of the lifespan of moving parts, such as bearings, by reducing temperatures of friction surfaces and improving abrasive resistance, thus reducing wear of their moving parts by using the present lubricant composition as mentioned above can surprisingly be improved by omitting conventional sulfur and/or phosphorus containing anti-wear and extreme pressure additives.

The compositions of this invention are used principally in the formulation of bearing greases and in the formulation of chassis greases, and comprise a major amount of an oil of lubricating viscosity, a thickener, the metal salts and the abrasive particles as described above, and optionally other additives as needed to provide the grease composition with the required properties.

Preferably, a lubricating grease may stimulate vibrations in the roller bearing which are in the medium-frequency band from 300 to 1800 Hz and high-frequency band 1800 to 10,000 Hz in revolving participation (rolling over, milling).
in comparison with the bearing noise in the low-frequency band at 50 to 300 Hz. Superimposed on the lubricant noise are sound peaks occurring with rollover of hard particles by the roller bearing in the form of shock pulses on the bearing ring. The sound performance is evaluated according to the SKF BeQuiet method based on a static analysis of the noise peaks and the assignment to the noise classes BQ1 to BQ4. With increasing values of the noise class, the noise behavior becomes worse and the lifetime of the roller bearing is shortened (H. Werries, E. Paland, FVA study of the topic "Low-noise lubricating greases," University of Hanover 1994). Thus, 100% noise class BQ1 characterizes a very good noise behavior and low percentage values exclusively in noise class BQ4 characterize very poor noise behavior.

[0123] The better the noise behavior of a lubricating grease, the lower are the vibrations of the bearing induced by the lubricant. This is equivalent to a low load on the bearing and leads to a longer service lifetime of the bearing.

[0124] The better the noise behavior of a lubricating grease, the lower are the vibrations of the bearing induced by the lubricant. This is equivalent a low load on the bearing and leads to a longer service lifetime of the bearing.

[0125] In general, the grease composition according to the present invention can be manufactured by any techniques known in the field, such as conventional mixing techniques, the different variations thereof being well known for those skilled in the art. Lubricating greases may be produced in batch processes or by continuous processes.

[0126] Preferably, the metal salts and/or the abrasive particles can be mixed with the base oil before the thickener is added to the base oil in order to achieve a grease composition of the present invention.


[0128] According to a preferred embodiment, the present grease composition can be prepared by first dispersing or mixing the thickener in the lubricating oil for from about 1 to about 8 hours or more (preferably from about 1 to about 4 hours) followed by heating at elevated temperature (e.g., from about 60 °C to about 260 °C depending upon the particular thickener used) until the mixture thickens.

[0129] Furthermore, continuous processes are known to prepare grease compositions as described, e.g. in US 2007/191238A1. The document US 2007/191238A1 is expressly incorporated herein by reference for its disclosure regarding the preparation of grease compositions by continuous processes.

[0130] The present greases can be used especially as bearing grease and/or as chassis grease.

[0131] The mechanical component having a metal surface to be treated with the grease composition according to the present invention is preferably a bearing, bearing component or a bearing application system. The bearing component may be inner rings, outer rings, cages, rollers, balls and seal-counter faces. The bearing application system in accordance with the present invention comprises bearing housings, mounting axles, shafts, bearing joints and shields. Further uses of the lubricant grease compositions according to the present invention are e.g. agricultural machinery, bearings in dam-gates, low noise electric motors, large size electric motors, fans for cooling units, machine tool spindles, screw conveyors, and offshore and wind turbine applications.

[0132] The following examples illustrate the invention further without any intention that this should impose a restriction.

Example 1 and Comparative Example 1

[0133] Comparative tribological tests were carried out comparing the efficiency of a metal plating grease composition (Metalplaks-Ps) as Comparative Example 1. The lubricating grease Metalplaks-Ps has as a basis a compound of mineral and synthetic oils thickened with lithium soaps of fatty acids and oxyacid and comprises an additive composition, which provides enhanced anti-friction and protective properties. The lubricating grease Metalplaks-Ps is commercially available under the trade name Metalub SS EP2 (MeTaΠΟΟΕ SS EP2) from Nanol Technologies, 111398 Moskau, ul. Kuskovskaya, 16A, Office 26. As Example 1, a composition comprising the prior art metal plating grease composition according to Comparative Example 1 (Metalplaks-Ps ) and an additional content of abrasive particles has been prepared (about 0.0006 wt. % having a hardness of at least 7 on the Mohs scale). The abrasive particles comprise boron carbide particles having an average diameter size of the boron carbide particles varied from 1μm to 3μm.

[0134] The comparative tests were conducted by a special procedure by loads of 700 MPa and 2600 MPa. The essence of the procedure is a tribological examination of the conjunction with a point contact provided by a sample (disc) rotating at a constant velocity and a stationary motionless counterbody (ball) at a constant load with heat emission registered during and at the end of the tests and it being an indicator of the heat emission rate.

[0135] During the test a raceway in form of a ring is developed on the disc surface and a contact spot is developed on the ball.

[0136] The parameters measured:

- The mass attrition (Δm, mg) of the sample and the counterbody in the given time at the defined load - determined by weighing the sample and the counterbody before and after the tests,
- The heating temperature of the counterbody (t, °C) - determined with the help of a thermocouple,
The wear spot of the ball (diameter $D_u$, mm) after the tests - determined with the help of a microscope.

[0137] The mass and linear wear of the friction pair depends on the type of the lubricant, the load ($P_{\text{general}}$, kg; $G_{\text{max,start}}$, kg/sm²), the contact load ($P_c$, kg/mm²) and the material of the friction pair.

[0138] By the point contact the heat emission in the friction area is dependent on the friction coefficient of the modified friction layer, heat conductivity and the thickness of the grease layer. The measured temperature (or the changed values of it) of one of the conjugated friction bodies during the tests is used to evaluate the type of change of the friction coefficient (positive or negative growing tendency), a change in the thickness of the lubricating grease layer as a function of the friction path length, of the testing period, of the lubricating grease material and of the friction pair.

1. Equipment and materials

[0139] 1.1. Testing samples are made in form of a flat disc from steel ShH 15 (a standard roller bearing steel having a chromium content of about 1.5 wt.%) with the diameter of $24 \pm 0.5$ mm, the height of $3.5 \pm 0.5$ mm, the hardness of HRC 62-64, non-parallelity of the working surfaces of no more than 0.1 mm and the roughness of the working surfaces of the samples $R_a \leq 0.63$ μm.

1.2. The counterbody is a ball from steel ShH 15 with the diameter of $6.3 \pm 0.05$ mm according to Russian Federal Standard ІОCT 3722 and the hardness of HRC 61-62.

1.3. The friction machine for testing of wear resistance (Pic. 1) provides the following testing conditions:

- Rotation rate of the shaft with the sample mounted on it $n=1400$ min⁻¹ ($V_{\text{lin}}=1.5$ m/s);
- Radial wobbling no more than 0.1 μM;
- Load $P_{\text{gen}}$ (contact tightness force) is adjusted with the loads of 0.124 kg to 6.32 kg depending on the working conditions of the friction unit according to the requirements specification;
- Nonstop registration of the thermo- electromotive force $E$, mV, with the help of a universal millivoltmeter $\hat{U}$68002-01 connected with the counterbody via thermocouple XK0, 3.

1.4. Microscope MBS-3 with the eyepiece with the magnification of $4 \times 8$ and more

1.5. Laboratory scales VLR-200г-M with the weighing inaccuracy of $\pm 0.05$ (± 0.00005 g) with the set of weights according to Russian Federal Standard ІОCT 73328-82

1.6. Washing liquids for the samples:
- benzine according to Russian Federal Standard ІОCT 443
- ethyl alcohol according to Russian Federal Standard ІОCT 18300

1.7. Stopwatch

2. Preparation for the tests

2.1. The sample in test and the counterbody are washed in alcohol, dried in the air and weighed with a weighing inaccuracy of no more than $\pm 0.00005$ g ($m_1, m_2$, g). The weighing is conducted three times with the scales’ null-position checking each time.

2.2. The testing sample is set in a holder (7) and fastened with hold-down screws.

2.3. The ball is fastened in the collet fixture (6) connected via thermocouple with the millivoltmeter.

2.4. Prior to launching the test the lubricating grease is laid on the disc with a palette knife or a syringe. The thickness of the lubricating layer should be sufficient for a visual detection of it across the whole working surface of the sample. After that the ball is set on the sample in accordance with Par. 2.3.

2.5. The load and the time period of the testing are chosen in accordance with the working conditions of the parts in the friction units (the settled friction mode on the given friction machine comes up to 1 hour).

The calculation of the needed load for achievement of the indicated tensions was conducted by the formula:

$$G_{\text{max}}=6568 \times \sqrt[3]{P_{\text{general}}} \times \frac{1}{r^2},$$

where $r$ is the radius of the ball.

3. Conduction of the tests
3.1. The settled value on the millivoltmeter at the initial time $E_0$, MV, is fixed (with the disc not rotating).

3.2. The driving gear of the apparatus is set on.

3.3. The readings of the millivoltmeter $E_x$, mV, are taken in time lapses of 5 s, 10 s, 15 s, 30 s, 45 s, 1 min and so on according to Table 1. Every 30 s small amounts of lubricating grease are added with a syringe onto the disc, or every 1-2 min. The added amounts of lubricant about 0.05-0.1 g are distributed across the radius of the disc with the help of a plastic palette knife.

3.3.1. After each testing period the sample in test and the counterbody are washed in alcohol or benzine, dried in the air, wiped with a cotton napkin and weighed with weighing inaccuracy of $\pm 0.00005$ g ($m_1$; $m_2$, g).

3.3.2. With the help of the microscope the width of the path on the disc is measured and the look/condition of the path profile is evaluated.

4. Processing of the results

4.1. The mass attrition of the surfaces of the sample $\Delta m_1$, g, and of the counterbody $\Delta m_2$, g, are determined as a difference of the weights of the sample and the counterbody before and after the testing.

$$\Delta m_1 = m_1 - m'_1,$$

$$\Delta m_2 = m_2 - m'_2,$$

the total mass attrition: $m = \Delta m_1 + \Delta m_2$

4.2. The contact (specific) load is calculated by the formula:

$$P_c = P_{\text{general}} / S, \text{ kg/mm}^2,$$

where $P_{\text{general}}$ is the load on the sample, kg;

$S$ is the area of the wear spot on the ball, mm$^2$,

$S = \pi D^2/4$.

The contact load allows evaluating the load capacity of the friction pair.

4.3. The friction power after the tests is calculated by the formula

$$W = P_c \times 10 \times V_{\text{lim}},$$

$P_c \times 10$ - contact (specific) load in MPa,

$V_{\text{lim}}$ - the linear rotation rate of the sample, m/s.

4.4. An increment in the temperature of the counterbody $t_x$, 0 °C, is calculated by the formula

$$\Delta t_x = 15.0777 \times (E_x - E_0), \text{ where } 15.0777 \text{ is the constant coefficient of the thermocouple XK 0,3 determined by calibration.}$$

4.5. The heat emission rate at the given moment of time (Table 1) is calculated by the formula:

$$\Delta t_y / \Delta t = \Delta t_x / \Delta t^0 / \text{min},$$
where $\Delta t$ is an increment in the temperature

$\Delta T$ is the time point at the given moment of time of the test according to Table 1.

4.6. For comparative evaluation of the wear capacity of the lubricant and the friction pairs as well as of their loading capacity and the type of the working/attrition mode the following function graphs are put up:

$$
\sum m; Du; P_c; \Delta t_{\text{final}}; \Delta t/\Delta T
$$
as a function of the load $P_{\text{general}}$, kg, of $T_{\text{test}}$, min, of the composition of the lubricant and so on.

[0140] The test results are given in Table 1:

<table>
<thead>
<tr>
<th>Type of lubricant</th>
<th>Load $P_{\text{general}}$, kg</th>
<th>Total mass attrition of the friction pairs $\sum m$, mg</th>
<th>Diameter of wear spot of the ball $Du$, mm</th>
<th>Loading capacity of the friction pair $P_c$, kg/mm$^2$</th>
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</thead>
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<tr>
<td>Example 1</td>
<td>1600</td>
<td>0.1</td>
<td>0.25</td>
<td>26.9</td>
</tr>
<tr>
<td>Metalplaks-Ps</td>
<td>2600</td>
<td>-0.05</td>
<td>0.6</td>
<td>22.6</td>
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<tr>
<td>Abrasive particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td>1600</td>
<td>0.15</td>
<td>0.25</td>
<td>26.9</td>
</tr>
<tr>
<td>Example 1</td>
<td>2600</td>
<td>-0.15</td>
<td>0.65</td>
<td>19.2</td>
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<tr>
<td>Metalplaks-Ps</td>
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Table 1: Test results (continuation)

<table>
<thead>
<tr>
<th>Type of lubricant</th>
<th>Heat emission rate $\Delta t/\Delta T$, °C/min</th>
<th>Working/Attrition time, min</th>
<th>Final heat emission</th>
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<tr>
<td></td>
<td>0.083</td>
<td>0.16</td>
<td>0.25</td>
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<td>-0.36</td>
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<td>0.18</td>
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<td>Metalplaks-Ps</td>
<td>1.63</td>
<td>2.26</td>
<td>2.41</td>
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<td>Abrasive particles</td>
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<td>0.18</td>
<td>0.47</td>
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<tr>
<td>Comparative</td>
<td>3.81</td>
<td>3.77</td>
<td>6.8</td>
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<tr>
<td>Example 1</td>
<td></td>
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</tr>
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</table>

[0141] In addition thereto, the test results are shown in Figures 1 to 5, wherein

- Figure 1 shows the total mass attrition of the friction pairs,
- Figure 2 shows the diameter of wear spot of the ball,
- Figure 3 shows the loading capacity of the friction pairs,
- Figure 4 shows the heat emission rate at 1600 MPa,
- Figure 5 shows the heat emission rate at 2600 MPa, and
- Figure 6 shows the final heat emission rate.

[0142] Conclusions from the results of the tribological tests of the lubricants Comparative Example 1 (Metalplaks-Ps) and Example 1 (Metalplaks-Ps with abrasive particles):

- The mass attrition of the friction pairs with the lubricant Metalplaks-Ps with abrasive particles has decreased by 3 times by the load of 2600 MPa,
- The loading capacity of the friction pairs with lubricant Metalplaks-Ps with abrasive particles has increased by 1.17 times by the load of 2600 MPa,
- The final heat emission rate has diminished by 1.3 times by the load of 2600 MPa.
Claims

1. A grease composition comprising a base oil component, at least one thickener and at least one metal salt, characterized in that the grease composition comprises at least one metal salt of an organic acid and at least one metal salt of an inorganic acid and from 0.00005 wt% to 0.01 wt%, preferably from 0.0001 wt% to 0.005 wt%, most preferably from 0.0001 wt% to 0.003 wt% abrasive particles.

2. Grease composition according to claim 1, characterized in that wherein the grease composition comprises at most 0.2 wt%, especially at most 0.1 wt%, preferably at most 0.05 wt%, more preferably at most 0.03 wt%, more preferably at most 0.02 wt% and most preferably at most 0.01 wt% of sulfur.

3. Grease composition according to any of claims 1 to 2, characterized in that the grease composition comprises at least one viscosity index improver.

4. Grease composition according to any of claims 1 to 3, characterized in that the average diameter size of abrasive particles ranges from 0.5 μm to 20 μm, preferably from 1 μm to 10 μm, most preferably from 1 μm to 3 μm.

5. Grease composition according to any of claims 1 to 4, characterized in that abrasive particles have a hardness of at least 7 on the Mohs scale.

6. Grease composition according to any of claims 1 to 5, characterized in that abrasive particles comprise carbonates, nitrides, carbides and/ or oxides of elements of boron, carbon and/ or alkaline earth metal groups.

7. Grease composition according to any of claims 1 to 6, characterized in that the grease composition comprises a NLGI consistency number according to DIN 51818 from 00 to 6, preferably from 0 to 6 and more preferably from 1 to 5.

8. Grease composition according to any of claims 1 to 7, characterized in that the grease composition comprises a thickener on the basis of soap.

9. Grease composition according to any of claims 1 to 8, characterized in that the grease composition comprises a thickener on the basis of a polymer.

10. Grease composition according to any of claims 1 to 9, characterized in that the grease composition comprises an inorganic thickener.

11. Grease composition according to any of claims 1 to 10, characterized in that the thickener is a lithium soap or a lithium complex soap prepared from hydroxy fatty acid having from 12 to 24 carbon atoms.

12. Grease composition according to any of claims 1 to 11, characterized in that the grease composition comprises a drop point of at least 180°C according to DIN ISO 2176.

13. A method for producing a grease composition to any of claims 1 to 12 comprising mixing a base oil with at least one metal salt of an organic acid and at least one metal salt of an inorganic acid and from 0.00005 wt% to 0.01 wt%, preferably from 0.0001 wt% to 0.005 wt%, most preferably from 0.0001 wt% to 0.003 wt% abrasive particles and a thickener.

14. A bearing, preferably a wheel bearing or a roller bearing, comprising a grease composition according to any of claims 1 to 12.

15. A chassis comprising a grease composition according to any of claims 1 to 12.
Figure 1

Total mass attrition of the friction pairs

Figure 2

Diameter of wear spot of the ball
Figure 3

Loading capacity of the friction pair

Figure 4

Heat emission rate by load of 1600 MPa
## DOCUMENTS CONSIDERED TO BE RELEVANT

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The present search report has been drawn up for all claims

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**Place of search:** Munich  
**Date of completion of the search:** 5 October 2012  
**Examiner:** Greß, Tobias

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**CATEGORY OF CITED DOCUMENTS**
- **X:** particularly relevant if taken alone
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- **O:** non-written disclosure
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