

(19)



(11)

EP 4 484 526 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.01.2025 Bulletin 2025/01

(51) International Patent Classification (IPC):
C10M 109/00 ^(2006.01) **C10M 121/00** ^(2006.01)

(21) Application number: **23182298.2**

(52) Cooperative Patent Classification (CPC):
C10M 109/00; C10M 121/00; C10N 2020/077;
C10N 2030/06; C10N 2030/12; C10N 2050/10

(22) Date of filing: **29.06.2023**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(71) Applicants:
• **Antzutkin, Oleg N.**
973 53 Luleå (SE)
• **de la Presilla, Roman**
182 46 Enebyberg (SE)
• **Calderon Salmeron, Gabriel**
115 43 Stockholm (SE)
• **Filippov, Andrei**
977 52 Luleå (SE)
• **Glavatskikh, Sergei**
11545 Stockholm (SE)

(72) Inventors:
• **Antzutkin, Oleg N.**
973 53 Luleå (SE)
• **de la Presilla, Roman**
182 46 Enebyberg (SE)
• **Calderon Salmeron, Gabriel**
115 43 Stockholm (SE)
• **Filippov, Andrei**
977 52 Luleå (SE)
• **Glavatskikh, Sergei**
11545 Stockholm (SE)

(74) Representative: **Ehrner & Delmar Patentbyrå AB**
Götgatan 78
118 30 Stockholm (SE)

(54) **LUBRICANT COMPOSITIONS**

(57) The invention relates to a lubricant composition comprising:
5 - 99 wt% of a non-halogenated ionic liquid or a mixture of non-halogenated ionic liquids, 0 - 15 wt% of one or more non-halogenated additives for lubricants, and the balance of a non-halogenated ionic thickener with at

least 1 wt% of non-halogenated ionic thickener. The invention also relates to a lubricating compound based entirely on the lubricant composition and to a method of protective surface treatment of a component configured to be exposed to wear.

EP 4 484 526 A1

Description

TECHNICAL FIELD

[0001] The invention relates to a lubricant composition based on ionic liquids. The invention relates in particular to a lubricant composition used in an ambient temperature range from - 70 °C to at least 200 °C to function as a lubricant on components to decrease friction and wear, to prolong the operational lifetime of components and to protect components provided with this lubricant from corrosion.

BACKGROUND

[0002] The development of novel lubricant compositions is associated with fulfilling new and higher requirements for performance characteristics, such as lowering of friction and wear in a wide temperature range of operations at high loads, high speeds, providing electrical (ionic) conductivity, preventing corrosion of machine elements. The use of ionic liquids (ILs) in lubrication technology has been investigated extensively in recent years.

[0003] The use of ILs has some environmental, health and technical performance concerns for the sustainable society. In particular, most known compositions of ionic liquids no longer meet the aforementioned requirements for lubricants, because of the presence of halogens. The conventional presence of halides (F, Cl, Br, I) in IL-lubricant compositions makes IL-lubricant disadvantageous because of the corrosiveness of such compounds at steel surfaces, toxicity to humans and ozone-depletion activity of halogen-containing compounds and products of their decomposition.

[0004] Ionic liquids are defined as materials comprised of cations and anions and having melting points below 100 °C. Many ionic liquids have a low melting point or glass-transition temperature, so they are present as liquids at room temperature and even down to -70°C, hereinafter referred to as room temperature ionic liquids (RTIL). RTILs are of special interest, particularly in the field of tribology, for high vacuum instrumentation and space exploration devices, since RTILs can be implemented as neat liquids, such as base oils in lubricants or as additives. An important class of lubricants is greases. For example, more than 90 % of rolling element bearings are grease lubricated [Lugt, P.M., 2012, Grease lubrication in rolling bearings. John Wiley & Sons]. A grease is composed of a base oil and a thickener [ASTM D217-21a]. Functional additives are usually added to a grease to enhance wear and friction reducing properties, oxidation stability and corrosion protection. When RTILs are added to greases they may provide additional properties: electrical (ionic) conductivity that eliminates electrostatic potentials, minimising risks for electrical discharging between moving components in electric machinery. Specific RTILs for lubrication applications contain tribologically active elements, such as phosphorus, boron and sulfur, which are known for forming friction-reducing or/and anti-wear protective tribofilms on steel surfaces. RTILs may also contain different organic functional groups, such as alkyl-aromatic, aryl-phosphate or alkyl-phosphate molecular moieties, which are efficient radical trappers that brings additional beneficial antioxidant and anti-corrosive properties to RTIL-based lubricant compositions. Alkyl-phosphate compounds are also known as efficient flame retardants.

[0005] Ionic liquids have a negligible vapour pressure, are non-flammable and are often thermally stable to temperatures above 200 °C or even as high as 300-350 °C and are also capable of lubricating metal and non-metal surfaces at elevated temperatures. RTILs with halogens, when they decompose, may produce substances such as hydrofluoric acid (HF) and POF_3 , which are dangerous and even lethal for humans at ppm level concentrations in air.

[0006] US 8455407 B2 discloses a lubricating grease composition based on halogen-containing ionic liquids. Specifically, the used ionic liquids are comprised of fluorine-containing RTIL-based lubricants.

[0007] A problem with many conventional RTIL-based lubricants is that they, in themselves or by the products of their decomposition, may give rise to corrosion. Despite this, prior art in ionic lubricating greases is insistent on the use of halide containing formulations, likely dictated by the reliance on extensively researched and commercially available halide-containing ionic species and the difficulty of developing formulations that achieve desirable physical properties and tribological performance with lesser known ionic species that do not contain halogens.

[0008] It would be advantageous to achieve a composition overcoming, or at least alleviating, at least one or some of the drawbacks of the prior art.

SUMMARY OF THE INVENTION

[0009] An object of the invention is to provide a lubricant composition that provide anticorrosion properties and better lubrication than most conventional lubricants.

[0010] This object is achieved in accordance with the first aspect of the invention by means of a lubricant composition comprising:

- 5 - 99 wt% of a **non-halogenated** ionic liquid or a mixture of **non-halogenated** ionic liquids,

- 0 - 15 wt% of one or more conventional **non-halogenated** additives for lubricants and
- the balance of a **non-halogenated** ionic thickener, with a minimum of 1 wt% non-halogenated ionic thickener.

[0011] The fact that halogens are avoided in the lubricant composition eliminates many problems of conventional ILs, such as their corrosiveness and otherwise negative effects on the environment. The invention is based on the notion that a common negative effect of conventional ILs is due to the presence of halogens in such ionic liquids. Although, non-halogenated ionic liquid are priorly known per se, their use has been limited and it has not been known to produce lubricant comprised of solely non-halogenated components.

[0012] The **non-halogenated** ionic liquid or mixture of **non-halogenated** ionic liquids according to the invention may be comprised of ionic liquids having a cation selected from the group consisting of tetraalkylphosphonium, tetraalkylammonium, dialkylpyrrolidinium, dialkylpiperidinium, dialkylimidazolium, trialkylimidazolium with alkyl-groups substituents with the general formula C_nH_{2n+1} , wherein the value of $1 \leq n \leq 80$, and having an anion selected from the group consisting of 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate, (mandelato)(oxalato)borate, bis(benzilato)borate, bis(2-ethylhexyl)phosphate, bis(mandelato)borate, bis(oxalato)borate, bis(salicylato)borate, bis(malonato)borate, bis(succinato)borate, bis(glutarato)borate, bis(adipato)borate, dodecylsulfate, (2-ethyl-hexyl)sulfate, bis(R_1, R_2 -glycolato)borate, where $R_1 = H, -C_6H_5, -C_nH_{2n+1}$ with $1 \leq n \leq 80$ and $R_2 = H, -C_6H_5, -C_nH_{2n+1}$ with $1 \leq n \leq 80$.

[0013] According to specific embodiments of the invention the ionic **non-halogenated** thickener may be an ionic material made of:

- (i) lithium *n*-(hydroxy)stearate (*n*-HSA) thickener where the -OH group position is at the carbon $n = 2, 3, \dots, 18$, preferably at $n = 12$,
- (ii) calcium *n*-HSA thickener where the -OH group position is at the carbon $n = 2, 3, \dots, 18$, preferably at $n = 12$,
- (iii) aluminium *n*-HSA thickener where the -OH group position is at the carbon $n = 2, 3, \dots, 18$, preferably at $n = 12$,
- (iv) barium *n*-HSA thickener where the -OH group position is at the carbon $n = 2, 3, \dots, 18$, preferably at $n = 12$,
- (v) thickeners based on aforementioned (i)-(iv) with lithium, calcium, aluminum and barium complexes with adipic acid as an additive,
- (vi) thickeners based on aforementioned (i)-(iv) with lithium, calcium, aluminium and barium complexes with sebacic acid as an additive,
- (vii) ionic polyurea,
- (viii) calcium sulfonate or calcium sulfonate complex,
- (ix) lithium calcium sarkosyl complex, and alternatively
- (x) the aluminosilicate component of bentonite or montmorillonite or attapulgite minerals.

[0014] In embodiments of the invention the non-halogenated ionic thickener consists of or comprises anionic aluminosilicate components (nanosheets of minerals) of bentonite or montmorillonite or attapulgite minerals with tetraalkylphosphonium, tetraalkylammonium, dialkylpyrrolidinium, dialkylpiperidinium, di-(or tri-)alkylimidazolium cations with alkyl-groups substituents with the general formula C_nH_{2n+1} , wherein $1 \leq n \leq 80$.

[0015] Conventional **non-halogenated** additives for lubricants that may be used are, but are not limited to: an anti-corrosion agent, antioxidant, anti-wear agent, extreme pressure additive, friction reducing agent, agent to protect against metal influences, UV stabiliser, an organic or inorganic solid lubricant selected from graphite-based compounds, metal oxides, boron compounds, molybdenum compounds and phosphates.

[0016] However, the lubricant composition may also be free from additives.

[0017] The invention relates to non-Halogenated Ionic Liquid Lubricant Compositions (nHILLCs).

[0018] In embodiments of the invention the composition comprises a mixture of non-halogenated ionic liquids constituting at least 15 - 99 wt% of the lubricant composition, wherein the mixture of non-halogenated ionic liquids consists solely of ions (cations and anions), with glass-transition temperatures and melting points ranging from -70°C to $+200^\circ\text{C}$.

[0019] In embodiments of the invention the composition of the non-halogenated ionic liquid or the mixture of non-halogenated ionic liquids constitute at least 60 wt % of the lubricant composition, or even 70 wt %, 80 wt % or 90 wt % may be advantageous in some embodiments.

[0020] In embodiments of the invention, the lubricant compositions consist of a fluid ionic phase and an ionic thickener, both consisting of solely ions and both lacking halogen-containing (i.e. F, Cl, Br, I) compounds in their structure, i.e. neither any ionic liquid component, nor an ionic additive, nor an ionic thickener contain halogen atoms down to measurable impurities of 2000 mg/kg that is 0.2 wt%, i. e. 2000 part-per-million (ppm), preferably 100-1000 mg/kg (100-1000 part-per-million, 0.01 - 0.1 wt%) levels. Halogen-containing compounds are excluded because, apart from environmental hazards, they cause the formation of corrosive species in the tribological contacts.

[0021] In embodiments of the invention, the lubricant composition, additives excluded, is comprised of a mixture of one or more of the following non-halogenated ionic liquid or liquids and the ionic thickener:

- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of a mixture of (90 wt% trihexyl(tetradecyl)phosphonium bis(mandelato)borate with 10 wt% trihexyl(tetradecyl)phosphonium bis(oxalato)borate) and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of a mixture of (50 wt% trihexyl(tetradecyl)phosphonium bis(mandelato)borate with 50 wt% trihexyl(tetradecyl)phosphonium bis(oxalato)borate) and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(salicylato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium (mandelato)(oxalato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of triethyl(octyl)phosphonium bis(mandelato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trioctyl(hexadecyl)phosphonium 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(benzilato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(2-ethyl-hexyl)phosphate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(oxalato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and 5-30 wt% Ca-12HSA thickener;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of azelaic acid, prepared by a one-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of azelaic acid, prepared by a two-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of sebacic acid, prepared by a one-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of sebacic acid, prepared by a two-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(oxalato)borate and a complex thickener composed of 5-30 wt% Ca-12HSA and 1-10 wt% calcium complex of azelaic acid, prepared by a one-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(oxalato)borate and a complex thickener composed of 5-30 wt% Ca-12HSA and 1-10 wt% calcium complex of sebacic acid, prepared by a one-step method. Specific exemplary compositions are given in the description of specific embodiments.

[0022] Non-Halogenated Ionic Liquid Lubricant Compositions have negligible volatility, which is one of the main requirements of lubricants for space and ultrahigh-vacuum-based applications. In one application body of this invention, nHILLCs could be used as lubricants with high ionic conductivity to prolong the lifespan of moving parts in electric machinery elements, generators and electric vehicles. nHILLCs based on non-halogenated ionic liquids (ILs) have an outstanding lubrication performance (low friction and low wear) in various lubricated contacts including fretting steel-steel contacts.

[0023] Lubricant technology is crucial for efficient and long-term operation of machinery. However, ionic liquids (ILs), as previously defined molten salts with melting point below 100 °C and room-temperature ionic liquids (RTILs), i.e. ILs with melting point below 20 °C yet did not reach the market as neat lubricants or/and as additives to lubricants, despite IL's unique "enabling" properties in a variety of tribological application, i.e. reduction of friction and wear in tribological contacts. A specific class of lubricants are greases, which are compositions of a liquid lubricant and a thickener. The market for

greases covers a wide range of types of machinery, from kitchen appliances to vehicles, trains, ships, and planes to wind power turbines.

[0024] nHILLCs are particularly necessary for electric vehicles, trains, generators, and other machinery and devices, where electrostatic discharges and arcing between moving elements may severely damage surfaces in friction, thus, decreasing the lifetime of machinery. The market of fully electric vehicles and wind power stations has been growing fast during the last two decades. It will grow even further during the transition from fossil-based to solely "green"-energy-sustainable society.

[0025] nHILLCs in this invention include:

(i) greases made of fully ionic components including neat ILs as base oils and fully ionic thickeners, such as lithium, calcium, aluminium, barium salts of anions of non-halogenated organic acids, their complexes with adipic and sebacic acids, ionic polyurea, calcium sulfonate, calcium sulfonate complex, lithium calcium sarkosylic complex or

(ii) a composition of ILs with the anionic aluminosilicate component of bentonite or montmorillonite or attapulgite, in which hydrophilic/hydrated metal ions (sodium or calcium) are substituted with a hydrophobic cation of an IL.

[0026] This invention presents examples of a number of preparation protocols for nHILLCs composed of neat ionic liquids and ionic thickeners-salts based on 12-(hydroxy)stearate anion with or without azelate or sebacate dianion and lithium or calcium cations, or the anionic aluminosilicate components (nanosheets of minerals) of bentonite or montmorillonite or attapulgite with tetraalkylphosphonium or tetraalkylammonium or dialkylpyrrolidinium or dialkylpiperidinium or dialkylimidazolium or trialkylimidazolium cations as thickeners.

[0027] nHILLCs are ionic non-halogenated materials, i.e. they mainly or completely consist of ions, contrary to commercially available and patented greases, which are mixtures of ionic and molecular components.

[0028] The invention also involves nHILLCs with properties of greases based on a lithium salt of 12-hydroxystearic acid (12-HSA) or with the hydroxyl (-OH) group at a carbon in any other position of the alkyl-chain of *n*-HSA with *n* = 2, 3, 11, 13,...18, or a calcium salt of 12-HSA (or with the hydroxyl (OH) group at a carbon in any other position of the alkyl-chain of *n*-HSA with *n* = 2, 3, 11, 13,...18) with or without lithium (or calcium) complexes with either azelaic or sebacic acids as thickeners after the saponification reactions.

[0029] Some principal features of the invention are:

- ionic liquid or a mixture of ionic liquids fully replace a non-ionic base oil generally used in commercial greases,
- non-halogenated ionic liquids are used, and halogenated ionic liquids are avoided. Further, in specific embodiments of the invention, solely ionic additives are considered, which could be either other ionic liquids or ionic salts.

[0030] Preparation protocols in this invention may result in nHILLCs, which are non-halogenated and consist of solely ions, i.e. non-halogenated IL or a mixture of non-halogenated ILs as a base-oil, a fully ionic non-halogenated thickener and fully ionic non-halogenated additives. The final product, nHILLCs, is made highly hydrophobic and traces of water are removed by thorough drying in a vacuum oven after the saponification reactions, specific examples of which are given below.

[0031] In embodiments of the invention, the nHILLCs are prepared from mixtures of non-halogenated ionic liquids with different glass-transition temperatures and melting points. One non-halogenated ionic liquid preferably has a low glass-transition temperature, below -50°C, while another non-halogenated ionic liquid has a high melting point, preferably above + 120°C, but even up to + 140°C or + 160°C.

[0032] Even a mixture of three or more non-halogenated ionic liquids, with different glass transition temperatures and melting points, can be prepared with various compositions with non-halogenated thickeners to adjust rheological and "oil"-bleeding properties for desired applications.

[0033] A homogeneous mixture of nHILLCs is prepared by a complete dissolution of non-halogenated ILs in a solvent (usually DCM or ethyl acetate), a thorough mixing of this solution assisted by a water-bath ultrasonication to ensure a homogeneous dissolution of all components in the solution. After homogenisation, the mixture is instantly frozen in liquid nitrogen and then lyophilised under vacuum to remove all the solvent (DCM or ethyl acetate). The resulting homogenised mixture of non-halogenated ILs is a wax-like nHILLC, in which the matrix is formed by a network of ions from a non-halogenated ionic liquid component having a high melting point (preferably above + 120°C), while channels with voids in this matrix are filled with another non-halogenated ionic liquid component, which has a low glass-transition temperature (preferably, below -50°C).

[0034] One specific example of nHILLCs based on solely mixtures of non-halogenated ionic liquids is a mixture of two tetraalkylphosphonium based ionic liquids (for example, with trihexyl(tetradecyl)phosphonium, $[P_{6,6,6,14}]^+$, cation) having anions with very different chemical functional groups, such as bis(oxalato)borate, $[BOB]^-$, and bis(benzilato)borate, $[BBB]^-$.

(see Fig. 1). [BOB]⁻ has four polar >C=O moieties around the orthoborate BO₄ core, while [BBB]⁻ has only two polar >C=O moieties around the orthoborate BO₄ core and four phenyl chemical groups.

[0035] As a result of these structural differences, [P_{6,6,6,14}][BOB] is a room-temperature non-halogenated IL (RTIL) having a glass transition temperature at -71 °C [M.R. Shimpi et al., Physical Chemistry Chemical Physics, 23 (2021) 6190], while [P_{6,6,6,14}][BBB] is a solid non-halogenated ionic material at room temperature, having a melting point above 80 °C. Therefore, a homogeneous mixture of [P_{6,6,6,14}][BOB] with [P_{6,6,6,14}][BBB], which was prepared using the aforementioned protocol, is a fully ionic non-halogenated wax-like material at near-room temperatures with a solid phase formed by [P_{6,6,6,14}][BBB] via interactions of phenyl groups of neighbouring anions and alkyl groups of the [P_{6,6,6,14}]⁺ cations, with channels and voids filled with liquid [P_{6,6,6,14}][BOB] (and some amounts of [P_{6,6,6,14}][BBB] dissolved in it) in the temperature range between ca. -70 °C and <80 °C). Upon shear of this material in a tribocontact the liquid phase ([P_{6,6,6,14}][BOB] with some amounts of [P_{6,6,6,14}][BBB]) bleeds out and facilitates an outstanding tribological performance of this nHILLCs, i.e. decreased friction and reduced wear. Viscoelastic properties of this non-halogenated ionic liquid mixture can be further adjusted by the addition of non-halogenated thickeners.

[0036] nHILLCs with different compositions of two, three or more non-halogenated ILs in homogenised mixtures can be prepared for different applications with desired rheological and oil-bleeding characteristics.

[0037] According to a second aspect the invention relates to a lubricating compound based entirely on the lubricant composition as described above.

[0038] The lubricating compound is preferably a semisolid colloidal lubricating compound, having a grease-like consistency with an NLGI 000 up to NLGI 6 comprised of a mix of liquid and a solid phase, or a wax-like semisolid phase.

[0039] Further, the lubricating compound may comprise a liquid phase and a solid phase and have a grease-like consistency with an NLGI between 1 and 3, where the liquid phase separation, according to ASTM D6184-22, corresponds to 0.1% to 50% of the total mass of the compound.

[0040] The lubricating compound may comprise a liquid phase and a solid phase and have a grease-like consistency such that penetration of the lubricant composition by a cone penetrator, according to ASTM D217-21a, corresponds to the range of 85 to 475 tenths of a millimetre.

[0041] The lubricating compound may comprise a liquid phase and a solid phase where the lubricant composition's storage modulus (G') is larger than its loss modulus (G'') at a certain shear stress and the opposite is true upon an increase of shear stress.

[0042] According to a third aspect the invention relates to the use of the lubricating compound as defined above as a lubricating and/or protective surface treatment on a component configured to be exposed to wear, the lubricating compound being provided to the surface of said component.

DRAWINGS

[0043] Below, the invention will be described with reference to drawings of which:

Fig. 1. Illustrates a metal salt of the bis(oxalato)borate, [BOB]⁻, anion (left) and lithium salt of the bis(benzilato)borate, [BBB]⁻, anion (right),

Fig. 2. Illustrates a multi-functional non-halogenated ionic liquid (nHIL) based on the [MBPP]⁻ anion known as an efficient radical scavenger terminating polymer elongation reactions. This anion provides antioxidant and anti-corrosive properties to nHILLCs, while the phosphate groups polymerise into polyphosphates forming anti-wear tribofilms in tribo-tracks on steel surfaces.

Fig. 3. Illustrates representative examples of the rheological behaviour of two Li-nGILLCs greases.

SPECIFIC EMBODIMENTS OF THE INVENTION

Preparation of Lithium-IL greases as nHILLCs (Li-nHILLCs)

[0044] From 1.5 to 10 g of a non-halogenated ionic liquid (nHIL) was used in all preparations of lithium greases described below.

[0045] From 11 to 20 wt % of 12-hydroxystearic acid (12-HSA) was used of the total sample weight before the synthesis of greases, during which the saponification reaction resulted in [Li][12-HSA] and water.

[0046] Lithium hydroxide (LiOH) was used in the equimolar ratio to 12-HSA.

Preparation of Lithium-IL greases as nHILLCs**[0047]**

1. 12-HSA was mixed with a nHIL and heated at temperatures around 75 °C (for some nHILs, temperatures were around 100 °C) until the mixture formed a homogeneous transparent liquid.

2. LiOH(s) was dissolved in a small amount of milli-Q water (just enough to completely dissolve the base) at 75 °C.

3. The LiOH(aq) solution was then added to the hot mixture of 12-HSA with the nHIL under continuous stirring. The saponification reaction was spontaneous, and water was expelled out from a grease formed during this reaction.

4. Water was removed from the system by heating under vacuum or by heating with stirring.

[0048] A number of **Li-nHILLCs** (with different wt% of the thickener 12-HSA and Li(OH)) were successfully prepared for a variety of nHILs.

[0049] Non-halogenated orthoborate-based anions described below are known to have friction-reducing and anti-wear properties [F.U. Shah et al. Physical Chemistry Chemical Physics, 13 (2011) 12865-12873], and they readily approach positively charged steel surfaces in tribo-contacts upon friction.

[0050] The non-halogenated [MBPP]⁻ anion given below is known as an efficient radical scavenger terminating the elongation of a polymer chain in polymer chemistry. Thus, this anion provides antioxidant and anti-corrosive properties to nHILLCs, in which it is used as the principal component or in a mixture with other non-halogenated ILs.

[0051] Notations for cations and anions of non-halogenated ILs (nHILs) used in examples of successfully prepared greases given below are the following:

- 2,2'-Methylenebis(4,6-di-tert-butylphenyl)phosphate anion: [MBPP]⁻
- (mandelato)(oxalato)borate anion: [MOB]⁻
- Bis(benzilato)borate anion: [BBB]⁻
- Bis(2-ethyl-hexyl)phosphate anion: [BEHP]⁻
- Bis(mandelato)borate anion: [BMB]⁻
- Bis(oxalato)borate anion: [BOB]⁻
- Bis(salicylato)borate anion: [BScB]⁻
- Triethyl(octyl)phosphonium cation: [P_{2,2,2,8}]⁺
- Trihexyl(tetradecyl)phosphonium cation: [P_{6,6,6,14}]⁺
- Trioctyl(hexadecyl)phosphonium cation: [P_{8,8,8,16}]⁺

Examples of Li-nHILLCs greases**[0052]**

1. Li-nHILLC-(P66614-BMB, with Li(OH), 11 wt% 12-HSA, 75 °C)

2. Li-nHILLC-(P66614-BMB, with Li(OH), 20 wt% 12-HSA, 75 °C)

3. Li-nHILLC-90% P66614-BMB+10% P66614-BOB, with Li(OH), 11 wt% 12-HSA, 75 °C)

4. Li-nHILLC-(90% P66614-BMB+10% P66614-BOB, with Li(OH), 15 wt% 12-HSA, 75 °C)

5. Li-nHILLC-(50% P66614-BMB+50% P66614-BOB, with Li(OH), 20 wt% 12-HSA, 75 °C)

6. Li-nHILLC-(P66614-BScB, with Li(OH), 11 wt% 12-HSA, 75 °C)

7. Li-nHILLC-(P66614-MOB, with Li(OH), 20 wt % 12-HSA, 75 °C)

8. Li-nHILLC-(P2228-BMB, with Li(OH), 20 wt% 12-HSA, 75 °C)

9. Li-nHILLC-(P88816-MBPP, with Li(OH), 11 wt% 12-HSA, 75 °C)

10. Li-nHILLC-(P66614-BBB, with Li(OH), 11 wt% 12-HSA, 100 °C)
11. Li-nHILLC-(P66614-BEHP, with Li(OH), 20 wt% 12-HSA, 75 °C)
- 5 12. Li-nHILLC-(P66614-BOB with Li(OH), 11 wt% 12-HSA, 100 °C)
13. Li-nHILLC-(P66614-BOB with Li(OH), 15 wt% 12-HSA, 100 °C)
14. Li-nHILLC-(P66614-BOB with Li(OH), 20 wt% 12-HSA, 100 °C)
- 10 15. Li-nHILLC-(P66614-MBPP with Li(OH), 11 wt% 12-HSA, 100 °C)
16. Li-nHILLC-(P66614-MBPP with Li(OH), 20 wt% 12-HSA, 100 °C)

15 Preparation of Calcium-IL greases as nHILLCs (Ca-nHILLCs)

[0053] Calcium-based nHILLCs, Ca-nHILLCs, were prepared using the anhydrous method and Ca(OH)_2 instead of Li(OH). Instead of 1 mol of Li(OH), 0.75 mol of Ca(OH)_2 were used because both $\text{Ca}^{2+}(\text{aq})$ and $\text{Ca(OH)}^+(\text{aq})$ ions were formed during the saponification reaction. 12-HSA was dissolved in IL at 70 °C (for some nHILs, temperatures were around 100 °C). Ca(OH)_2 was added as small portions of a thin powder with intensive mixing. Finally, a homogeneous, but turbid liquid mixture was obtained. After cooling, the mixture formed a homogeneous grease. Samples were dried under low pressure at 75 °C for 6 hours. During drying, samples were mechanically agitated several times. The ^1H NMR signal from water (at 4.8 ppm) was not detected above the noise level in ^1H NMR spectra of such prepared samples of Ca-nHILLCs.

[0054] The following stable-over-time Ca-nHILLCs were successfully prepared:

17. Ca-nHILLCs-(P66614-BMB with Ca(OH)_2 , 11 wt% 12-HSA, 100 °C)
18. Ca-nHILLCs-(P66614-BMB with Ca(OH)_2 , 20 wt% 12-HSA, 100 °C)

30 Preparation of Lithium complex-IL greases as nHILLCs (LiX-nHILLCs)

[0055] Lithium-based greases with 12-HSA and azelaic (Az) or sebacic (Seb) acids were prepared by two methods, in two and/or one steps.

[0056] A two-step method (2): in the first step, greases were prepared from a nHIL and 11 wt% of 12-HSA with equimolar quantities of LiOH(aq). In the second step, a powder sample of Az or Seb acids (ca. 1/3 by weight of 12-HSA) was added and mixed in the grease at 80 °C. Finally, Az or Seb acids were neutralised by two-fold molar ratio of LiOH(aq). In the final step, water was removed in the oven, as in the case of Li-nHILLC preparations.

[0057] A one-step method (1): 11 wt% of 12-HSA and ca. 4 wt% of Az or Seb acid were mixed together and then added to a hot IL until the mixture became transparent. Then the acids were neutralised with corresponding amounts of LiOH(aq) as in the two-step method above. Preparations of LiX-nHILLCs systems containing sebacic acid were more challenging than LiX-nHILLC systems containing azelaic acid. It took around 48 h to dissolve sebacic acid grains in the IL.

[0058] The following stable-over-time LiX-nHILLCs were successfully prepared:

19. LiX-nHILLC-(P66614-BMB-Az(2), with Li(OH), 11 wt% 12-HSA, 4 wt% azelaic acid, 2 step reaction, 100 °C)
20. LiX-nHILLC-(P66614-BMB-Az(1), with Li(OH), 11 wt% 12-HSA, 4 wt% azelaic acid, 1 step reaction, 100 °C)
21. LiX-nHILLC-(P66614-BMB-Seb(2), with Li(OH), 11 wt% 12-HSA, 4 wt% sebacic acid, 2 step reaction, 100 °C)
22. LiX-nHILLC-(P66614-BMB-Seb(1), with Li(OH), 11 wt% 12-HSA, 4 wt% sebacic acid, 1 step reaction, 100 °C)

Preparation of Calcium complex-IL greases as nHILLCs (CaX-nHILLCs)

[0059] A grease was prepared from P66614-BOB, 12-HSA (11 wt %), azelaic acid (4 wt %, i.e. ca. 1/3 of 12-HSA) and Ca(OH)_2 using the anhydrous method: 12-HSA and azelaic acid were dissolved in P66614-BOB at 100 °C. Ca(OH)_2 was added in small portions as a thin powder with intensive mixing. The mixture was homogeneous during the preparation and after cooling. Samples were dried under low pressure at 75 °C for 6 hours.

[0060] A grease was prepared from P66614-BOB, 12-HSA (11 wt %), sebacic acid (4 wt %, i.e. ca. 1/3 of 12-HSA) and

Ca(OH)₂ using the anhydrous method. 12-HSA and sebacic acid were dissolved in P66614-BOB at 160 °C. Ca(OH)₂ was added in small portions as a thin powder with intensive mixing. The mixture was homogeneous during the preparation and after cooling. Samples were dried under low pressure at 75 °C for 6 hours.

23. CaX-nHILLC-(P66614-BOB-Az(1), with Ca(OH)₂, 11 wt% 12-HSA, 4 wt% azelaic acid, 1 step reaction, 100 °C)

24. CaX-nHILLC-(P66614-BOB-Seb(1), with Ca(OH)₂, 11 wt% 12-HSA, 4 wt% sebacic acid, 1 step reaction, 160 °C)

Rheological tests on Li-nHILLCs greases

[0061] A TA Instruments HR-3 Rheometer was used to evaluate if the manufactured Li/Ca-nHILLCs greases present the normal rheological behaviour of ordinary lubricating greases. A procedure based on the DIN 51810-4 standard was used for the evaluation. The procedure consisted of two parts. First, a tempering and relaxation step was performed. In this step, a Li/Ca-nHILLCs grease sample was applied with a spatula on the plate at 25 °C. Then, the upper geometry (cone diameter 20 mm, angle 0.9839°) was lowered to the "trimming" gap (73 µm), and the excess grease was removed carefully with the spatula. After this, the cone was lowered to the "geometry gap" (23 µm), and the sample was kept at rest for 10 minutes. The second step consisted of an oscillatory amplitude sweep with increasing strain (0.01 % to 1000 %) and a frequency of 10 rad/s.

[0062] The rheological results of the Li/Ca-nHILLCs greases exhibited a characteristic viscoelastic behaviour typical for a lubricating grease with the NLGI parameter ranging from 2 to 5 depending on the relative content of thickeners in the lubricating compositions.

[0063] Figure 3 presents the results of the storage modulus G' (elastic part) and the loss modulus G'' (viscous part) of two of the tested greases. At low shear or oscillation stress, the elastic behaviour of the grease dominates this region (G' > G''). This region, characterised by a plateau and a constant ratio of G' and G'', is known as the linear viscoelastic region (LVE). G' and G'' were calculated in this region for the tested greases. With increasing shear stress, G' starts decreasing, and the contribution of the viscous part becomes more dominant. The yield stress is the shear stress at which G' is 90% of the G' at the LVE. Finally, at high shear stresses, the viscous (liquid phase) contribution becomes more dominant (G' < G''), and the grease starts to flow. According to the DIN 51810-4 standard, the last four points of this region could be used for calculating an equivalent penetration consistency in metal-saponified greases. Table 1 presents the aforementioned calculated properties of the Li/Ca-nHILLCs greases.

Table 1. Rheological properties on Li/Ca-nHILLCs greases.

	G' LVE [Pa]	G'' LVE [Pa]	tan delta LVE	Yield stress [Pa]	Penetration DIN 51810-4 Pen60 [1/10 mm]	NLGI
Grease from 90 wt% P66614-BMB + 10 wt% P66614-BOB (Li(OH) with 15 wt % 12- HSA)	327297	51892	0.16	180	271	2
Grease from P66614-BMB (LiOH with 11 wt % 12-HSA)	39217	8736.9	0.2	48	290	2
Grease from P66614-BOB (Ca(OH) ₂ by the anhydrous method with 11 wt % 12- HSA)	464944	58919	0.13	381	254	2 to 3

Tribological tests on Li/Ca-nHILLCs greases

[0064] A tribological screening of the lubricious behavior of the non-Halogenated Ionic Liquid Lubricant Compositions (nHILLC) was conducted using a High Frequency Reciprocating Rig (HFRR) by PCS Instruments. The nHILLCs were used to lubricate a steel-steel ball-on-flat fretting contact while the frictional response was recorded. The ball specimen specification is in accordance with ASTM D6079, whereas the disc specimen differs in that it has a higher hardness (800 HV). The test was conducted at 26 °C and consisted of 500,000 fretting cycles at 50 Hz, with a 70 µm stroke, and a maximum Hertzian pressure of 1.4 GPa. Under such conditions, the occurrence of high friction events (instances where friction coefficient is greater than 0.2) are indicative of a critical lubricant failure and correspond to metal-metal contact and pronounced adhesive wear. The performances of the nHILLCs is reported in Table 2 in terms of the mean and standard

deviation of the friction coefficient and the amount of fretting cycles during high friction events. The standard deviation of the friction coefficient is an indicator of how stable the friction is, whereas the number of cycles during high friction events are indicative of the severity of the lubricant failure. Results indicate that many of the examined formulations showcase remarkable, and uninterrupted, lubricious behaviour even when compared to a commercial product intended for fretting applications.

Table 2. Friction coefficients and high friction event count for nHILLCs and a reference commercial grease subjected to a fretting test.

nHILLC	Mean Friction Coefficient (Standard Deviation)	Number of cycles with friction coefficient higher than 0.2
Commercial Anti-Fretting Grease (for reference)	0.13 (0.03)	5040
Grease from 90 wt% P66614-BMB + 10 wt% P66614-BOB (Li(OH) with 15 wt % 12-HSA)	0.129 (0.004)	0
Grease from P66614-BMB (LiOH with 11 wt % 12-HSA)	0.119 (0.004)	0
Grease from P66614-BOB (LiOH with 11 wt % 12-HSA)	0.123 (0.004)	0
Grease from P66614 85 wt % BMB + 15 wt % BOB (LiOH with 11 wt % 12-HSA)	0.111 (0.003)	0
Grease from P66614BOB (Ca(OH) ₂ by the anhydrous method with 11 wt % 12HSA and 4 wt % sebacic acid)	0.120 (0.004)	0
Grease from P66614 BEHP (Li(OH) with 20 wt % 12-HSA)	0.11 (0.02)	2,500

Preparation of nHILLCs with the anionic aluminosilicate components (nanosheets of minerals) of bentonite or montmorillonite or attapulgite minerals

[0065] One of the objects of this invention are nHILLCs with known properties of ionogels formed as a result of intercalation of a non-halogenated ionic liquid in-between negatively charged sheets of a montmorillonite mineral, which performs the function of a thickener and plasticiser for nHILLCs. Structures of sodium or calcium montmorillonites are stabilised by metal ions, usually sodium or calcium cations. However, these cations have hydrated shells with up to ca. eight-twelve or four-six water molecules, respectively. These ions cause hydrophilicity of Na- and Ca-montmorillonites, which easily absorb water and form a paste with specific rheological properties of a binder. In this invention, a thickener for nHILLCs is produced in Step 1 by substituting sodium or/and calcium cations with hydrophobic cations (Cat), such as tetraalkylphosphonium, tetraalkylammonium, dialkylpyrrolidinium, dialkylpiperidinium, di-(or tri-)alkylimidazolium cations in a metathesis reaction between Na/Ca-montmorillonite and halides of the aforementioned cations and by subsequent washings of Na/Ca halides from the reaction mixture giving rise to Cat-montmorillonite paste/thickener in the solvent of the metathesis reaction (usually, dichloromethane, DCM). In Step 2, a pre-selected non-halogenated ionic liquid is added to a DCM solution of Cat-montmorillonite, thoroughly mixed up and then DCM is rotor-evaporated giving rise to a nHILLCs with montmorillonite sheets forming a matrix of a thickener and the non-halogenated ionic liquid as a base oil lubricant.

[0066] The final product, nHILLCs, is fully ionic since all components of the montmorillonite and the ionic liquid consist of solely ions. The principal difference of the invention from previously reported arts, i.e. IL-based ionogels [A.V. Agafonov et al., Journal of Molecular Liquid, 315 (2020) 113703], is in substitution/washing off sodium, calcium (and other types of) metal ions from montmorillonite, which are hydrophilic, prone to absorption of water that may lead to corrosion at steel surfaces lubricated by IL-Na/Ca ionogels reported previously [A.V. Agafonov et al., Journal of Molecular Liquid, 315 (2020) 113703]. In the current invention, metal ions are substituted by hydrophobic non-halogenated cations, which are also compatible with hydrophobic ions in non-halogenated ionic liquids admixed to a solution of the thickener during Step 2 of the synthesis. The final system is then dried in a vacuum oven to remove traces of water left after metathesis/washings procedures of the final product, nHILLCs. The current invention protects different compositions of the non-halogenated Cat-montmorillonite thickener with a non-halogenated ionic liquid or a mixture of a few non-halogenated ionic liquids in the final product, nHILLCs, to achieve their desired rheological properties, oil bleeding points, high thermal stability, a good electrical conductivity combined with the outstanding tribological performance of nHILLCs. The latter does depend on friction and wear reducing properties of a non-halogenated IL (or a mixture of non-halogenated ILs), but also on the interaction between ions and montmorillonite sheets in these nHILLCs.

[0067] The invention is functional even with very small amounts of non-halogenated IL or a mixture of non-halogenated ILs in nHILLCs. Due to the interfacial properties, even small amounts of a tribologically active component, such as non-

halogenated ILs, could be sufficient to achieve the required properties at interfaces in tribotracks lubricated by nHILLCs, i.e. lowering of friction and wear and providing sufficient electrical conductivity to nHILLCs. These different nHILLCs could be semisolid colloidal materials as non-halogenated greases or non-halogenated wax-like semisolid materials.

[0068] Above, the invention has been described with reference to specific embodiments. The invention is however not limited to these embodiments. It is obvious to a person skilled in the art that other embodiments are possible within the scope of the following claims.

Claims

1. A lubricant composition comprising:

- 5 - 99 wt% of a non-halogenated ionic liquid or a mixture of non-halogenated ionic liquids,
- 0 - 15 wt% of one or more non-halogenated additives for lubricants and
- the balance of a non-halogenated ionic thickener, with a minimum of 1 wt% non-halogenated ionic thickener.

2. The lubricant composition of claim 1, comprising a mixture of non-halogenated ionic liquids constituting at least 15 - 99 wt% of the lubricant composition, wherein the mixture of non-halogenated ionic liquids consists solely of ions (cations and anions), with glass-transition temperatures and melting points ranging from -70°C to +200°C.

3. The lubricant composition according to anyone of the preceding claims, wherein the non-halogenated ionic liquid or the mixture of non-halogenated ionic liquids is/are comprised of ionic liquids having a cation selected from the group consisting of tetraalkylphosphonium, tetraalkylammonium, dialkylpyrrolidinium, dialkylpiperidinium, dialkylimidazolium, trialkylimidazolium with alkyl-groups substituents with the general formula C_nH_{2n+1} , wherein the value of $1 \leq n \leq 80$, and having an anion selected from the group consisting of 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate, (mandelato)(oxalato)borate, bis(benzilato)borate, bis(2-ethyl-hexyl)phosphate, bis(mandelato)borate, bis(oxalato)borate, bis(salicylato)borate, bis(malonato)borate, bis(succinato)borate, bis(glutarato)borate, bis(adipato)borate, dodecylsulfate, (2-ethyl-hexyl)sulfate, bis(R_1, R_2 -glycolato)borate, where $R_1 = H, -C_6H_5, -C_nH_{2n+1}$ with $1 \leq n \leq 80$ and $R_2 = H, -C_6H_5, -C_nH_{2n+1}$ with $1 \leq n \leq 80$.

4. The lubricant composition according to anyone of the preceding claims, wherein the non-halogenated ionic thickener is selected from the group consisting of:

- (i) lithium n-hydroxy-stearate (n-HSA) thickener where the -OH group position is at the carbon $n = 2, 3, \dots 18$, preferably at $n = 12$,
- (ii) calcium n-HSA thickener where the -OH group position is at the carbon $n = 2, 3, \dots 18$, preferably at $n = 12$,
- (iii) aluminium n-HSA thickener where the -OH group position is at the carbon $n = 2, 3, \dots 18$, preferably at $n = 12$,
- (iv) barium n-HSA thickener where the -OH group position is at the carbon $n = 2, 3, \dots 18$, preferably at $n = 12$,
- (v) thickeners based on aforementioned (i)-(iv) with lithium, calcium, aluminium and barium complexes with adipic acid as an additive,
- (vi) thickeners based on aforementioned (i)-(iv) with lithium, calcium, aluminium and barium complexes with sebacic acid as an additive,
- (vii) ionic polyurea,
- (viii) calcium sulfonate or calcium sulfonate complex, and
- (ix) lithium calcium sarkosylic complex.

5. The lubricant composition according to anyone of claims 1 - 3, wherein the non-halogenated ionic thickener comprises anionic aluminosilicate components (nanosheets of minerals) of bentonite or montmorillonite or attapulgite minerals with tetraalkylphosphonium, tetraalkylammonium, dialkylpyrrolidinium, dialkylpiperidinium, di-(or tri-)alkylimidazolium cations with alkyl-groups substituents with the general formula C_nH_{2n+1} , wherein $1 \leq n \leq 80$.

6. The lubricant composition according to anyone of the preceding claims, wherein the one or more non-halogenated additive is selected from the group consisting of an anti-corrosion agent, antioxidant, anti-wear agent, extreme pressure additive, friction reducing agent, agent to protect against metal influences, UV stabiliser, an organic or inorganic solid lubricant selected from graphite-based compounds, metal oxides, boron compounds, molybdenum compounds and phosphates.

7. The lubricant composition according to anyone of the preceding claims, wherein the lubricant composition comprises

solely ionic additives.

8. The lubricant composition according to anyone of the preceding claims, wherein the non-halogenated ionic liquid or the mixture of non-halogenated ionic liquids constitute at least 70 wt % of the lubricant composition.

9. The lubricant composition according to anyone of the preceding claims, wherein the lubricant composition, additives excluded, is comprised of a mixture of one or more of the following non-halogenated ionic liquid or liquids and the ionic thickener:

- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of a mixture of (90 wt% trihexyl(tetradecyl)phosphonium bis(mandelato)borate with 10 wt% trihexyl(tetradecyl)phosphonium bis(oxalato)borate) and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of a mixture of (50 wt% trihexyl(tetradecyl)phosphonium bis(mandelato)borate with 50 wt% trihexyl(tetradecyl)phosphonium bis(oxalato)borate) and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(salicylato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium (mandelato)(oxalato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of triethyl(octyl)phosphonium bis(mandelato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trioctyl(hexadecyl)phosphonium 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(benzilato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(2-ethyl-hexyl)phosphate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(oxalato)borate and 5-30 wt% Li-12HSA thickener;
- 70-95 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and 5-30 wt% Ca-12HSA thickener;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of azelaic acid, prepared by a one-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of azelaic acid, prepared by a two-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of sebacic acid, prepared by a one-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(mandelato)borate and a complex thickener composed of 5-30 wt% Li-12HSA and 1-10 wt% lithium complex of sebacic acid, prepared by a two-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(oxalato)borate and a complex thickener composed of 5-30 wt% Ca-12HSA and 1-10 wt% calcium complex of azelaic acid, prepared by a one-step method;
- 60-94 wt% of trihexyl(tetradecyl)phosphonium bis(oxalato)borate and a complex thickener composed of 5-30 wt% Ca-12HSA and 1-10 wt% calcium complex of sebacic acid, prepared by a one-step method.

10. A lubricating compound based entirely on the lubricant composition according to anyone of the preceding claims.

11. The lubricating compound of claim 10, which lubricating compound is a semisolid colloidal lubricating compound, having a grease-like consistency with an NLGI 000 up to NLGI 6 comprised of a mix of liquid and a solid phase, or a wax-like semisolid phase.

12. The lubricating compound according to claim 10 or 11, the compound comprising a liquid phase and a solid phase and having a grease-like consistency with an NLGI between 1 and 3, where the liquid phase separation, according to ASTM D6184-22, corresponds to 0.1% to 50% of the total mass of the compound.

13. The lubricating compound according to claim 10, 11 or 12, the compound comprising a liquid phase and a solid phase and having a grease-like consistency such that penetration of the lubricant composition by a cone penetrator, according to ASTM D217-21a, corresponds to the range of 85 to 475 tenths of a millimetre.

14. The lubricating compound according to anyone of the claims 10 - 13, the compound comprising a liquid phase and a solid phase where the lubricant composition's storage modulus (G') is larger than its loss modulus (G'') at a certain shear stress and the opposite is true upon an increase of shear stress.

15. Use of the lubricating compound according to anyone of the claim 10 - 14 as a lubricating and/or protective surface treatment on a component configured to be exposed to wear, the lubricating compound being provided to the surface

of said component.

5

10

15

20

25

30

35

40

45

50

55



Fig. 1

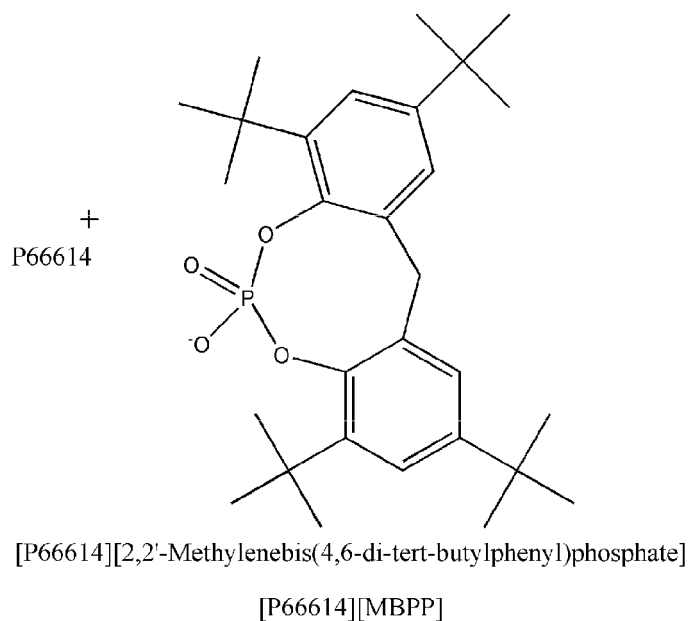


Fig. 2

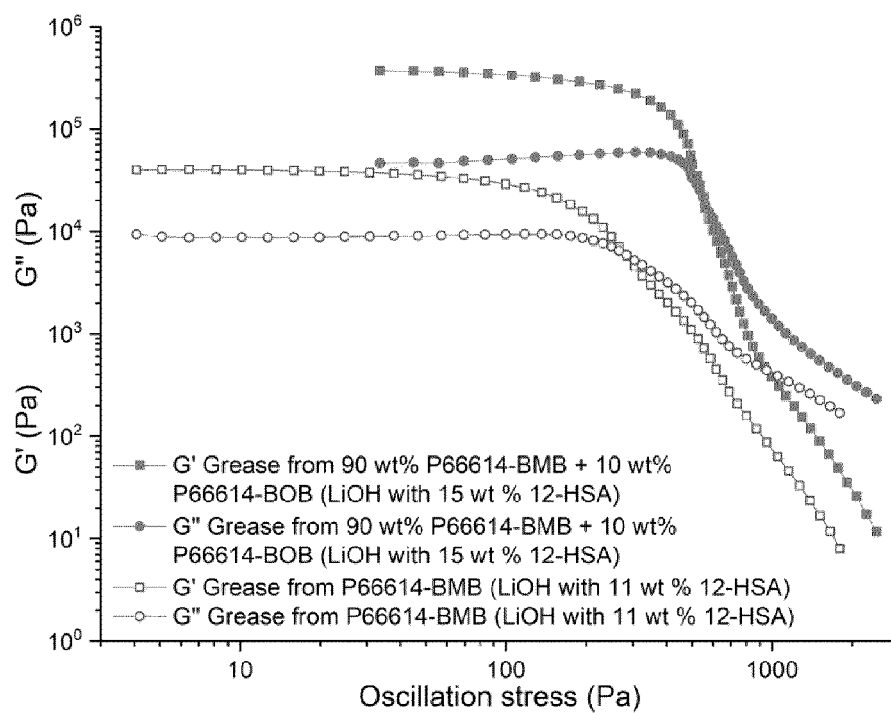


Fig. 3



EUROPEAN SEARCH REPORT

Application Number

EP 23 18 2298

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	QIN ZHAO ET AL: "Tribological Behavior of Protic Ionic Liquids with Dodecylamine Salts of Dialkyldithiocarbamate as Additives in Lithium Complex Grease", TRIBOLOGY LETTERS, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 48, no. 2, 12 July 2012 (2012-07-12), pages 133-144, XP035117612, ISSN: 1573-2711, DOI: 10.1007/s11249-012-0011-z	1, 4, 6, 7, 10-15	INV. C10M109/00 C10M121/00
A	* the whole document *	2, 3, 5, 8, 9	
X	JP 2020 193287 A (ENEOS CORP) 3 December 2020 (2020-12-03)	1, 2, 4, 6, 7, 10-15	
A	* paragraphs [0014] - [0017], [0022] - [0024], [0028] - [0037]; claims; figure 1; tables 1, 2 *	3, 5, 8, 9	
A	US 2011/092399 A1 (SCHMIDT-AMELUNXEN MARTIN [DE] ET AL) 21 April 2011 (2011-04-21) * claims; examples *	1-15	TECHNICAL FIELDS SEARCHED (IPC) C10M C10N
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 19 December 2023	Examiner Péntek, Eric
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 18 2298

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-12-2023

10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2020193287 A	03-12-2020	JP 7218242 B2	06-02-2023
		JP 2020193287 A	03-12-2020

US 2011092399 A1	21-04-2011	CN 101983231 A	02-03-2011
		DE 102008017144 A1	15-10-2009
		EP 2260091 A1	15-12-2010
		HK 1150621 A1	06-01-2012
		JP 5532265 B2	25-06-2014
		JP 2011518897 A	30-06-2011
		US 2011092399 A1	21-04-2011
		WO 2009121494 A1	08-10-2009

15

20

25

30

35

40

45

50

55

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 8455407 B2 [0006]

Non-patent literature cited in the description

- **LUGT, P.M.** Grease lubrication in rolling bearings. John Wiley & Sons, 2012 [0004]
- **F.U. SHAH et al.** *Physical Chemistry Chemical Physics*, 2011, vol. 13, 12865-12873 [0049]
- **A.V. AGAFONOV et al.** *Journal of Molecular Liquid*, 2020, vol. 315, 113703 [0066]