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(54) METHOD FOR PREPARING A LUBRICATING GREASE

(57) The present invention relates to a method for preparing a lubricating grease, particularly using a ball mill, and the lubricating grease obtained thereof.

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Description

Technical field

[0001] The present invention relates to a method for preparing a lubricating grease, particularly using a ball mill, and the lubricating grease obtained thereof.

Technical background

[0002] Lubricating greases, which are widely used for lubrication in various industries, usually at least comprise a base oil and a thickener. Such lubricating greases may be prepared by mixing the raw materials at a high temperature and applying a homogenization treatment.

[0003] Lubricating greases comprise mineral or synthetic oils as base oils, and metal-based (mainly lithium or calcium) soaps or polyurea compounds as thickeners are known. See, for example, the Japanese patent application JP 2019-127532 A.

[0004] In recent years, in an attempt to improve the human safety profile and to reduce their environmental load, without impairing the lubricating properties, alternative lubricating greases, at least partly derived from natural resources, have been provided. See, for example, the article from R. Gallego, et.al., ACS Sustainable Chem. Eng. 2015, 3(9), 2130-2141; the article from R. Gallego et al., Tribol. Int. 2016, 94, 652-660; the article from Antonio M. Borrero-López, et al., ACS Sustainable Chem. Eng. 2018, 6(4), 5198-5205; the European patent application EP 3677662 A1; the European patent application EP 3290497 A1; and the Japanese patent application JP 2013116991 A. While having an improved biodegradability profile, these lubricating greases are not entirely satisfactory.

[0005] Thus, there is a need for providing a lubricating grease having an improved human safety profile and a reduced environmental load, while having satisfactory lubricating properties, and the method for preparing it. There is also the need for providing a lubricating grease having an improved biodegradability profile, and the method for preparing it. There is also the need for providing a lubricating grease having satisfactory dispersibility, and the method for preparing it. There is also the need for providing a lubricating grease having satisfactory thermal stability and heat resistance, and the method for preparing it. There is also the need for providing a lubricating grease having satisfactory tribological properties, and the method for preparing it. There is also the need for providing a lubricating grease having satisfactory properties in terms of lubricity, stability, work penetration and/or wear resistance, and the method for preparing it. There is also the need for providing a lubricating grease having a simplified formulation. There is also the need for simplifying the method for preparing the lubricating grease. There is also the need for reducing the cost and the time for preparing the lubricating grease. There is also the need for reducing, or even avoiding, the thermal degradation of the materials upon preparing the lubricating grease.

Summary of the invention

[0006] In one aspect, the present invention relates to a method for preparing a lubricating grease, wherein the method comprises the following steps:

a) providing at least one natural base oil;
b) providing at least one unmodified natural thickening material;
c) ball milling the at least one natural base oil and the at least one unmodified natural thickening material for obtaining a lubricating grease.

[0007] In some embodiments, the step of ball milling is carried out using a ball mill; preferably a ball mill selected from the group consisting of a tumbler ball mill, a planetary ball mill, a vibrational ball mill and an attritor-stirred ball mill; preferably the ball mill is a planetary ball mill.

[0008] In some embodiments, the natural base oil is selected from the group consisting of vegetable oil, animal oil, and combinations thereof; preferably the at least one natural base oil is a vegetable base oil; more preferably the vegetable base oil is selected from the group consisting of almond oil, babassu oil, camellia oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, groundnut oil, linseed oil, mustard oil, olive oil, palm oil, peanut oil, rapeseed oil, rice bran oil, safflower oil, sesame oil, soybean oil, sunflower oil, tung oil, and combinations thereof.

[0009] In some embodiments, the at least one unmodified natural thickening material is obtained from the group consisting of bacteria, yeasts, fungi, plants, animals, and mixtures thereof; preferably the unmodified natural thickening material is a biomass by-product; more preferably the unmodified natural thickening material is a lignocellulosic material; still more preferably the lignocellulosic material is selected from the group consisting of barley straw, typha straw, rice straw, linen powder, and mixtures thereof.

[0010] In some embodiments, the at least one unmodified natural thickening material is a raw material or a purified material.

[0011] In some embodiments, the at least one unmodified natural thickening material is not chemically modified; preferably the unmodified natural thickening material is not chemically modified by carbamidation, carboxymethylation, crosslinking, etherification, esterification, epoxidation, functionalization, phosphorylation, oxidation, urethanization.

[0012] In some embodiments, the at least one natural base oil and the at least one unmodified natural thickening material are provided in a weight ratio of from 8:2 to 2:8.

[0013] In some embodiments, no solvent is provided.

[0014] In another aspect, the present invention relates to a lubricating grease obtained by the above method.

[0015] In another aspect, the present invention relates to a lubricating grease comprising:

a) at least one natural base oil; and
b) at least one unmodified natural thickening material;
wherein the lubricating grease has a penetration variation after working of from 0 to 20 dmm, a storage modulus G' value of from 10^1 to 10^7 Pa, and a loss modulus G" value lower than the G' value; and a friction coefficient at a load of 20N for 10 min of less than 0.1.

[0016] In some embodiments, the lubricating grease provides a wear mark resulting from a load of 20N for 10 min of less than 400 μm in diameter.

[0017] In some embodiments, the lubricating grease comprises from 20 to 80 %, preferably from 30 to 60 %, of the at least one unmodified natural thickening material, by total weight of the mixture of the natural base oil and the unmodified natural thickening material.

[0018] In some embodiments, the lubricating grease has an oxidation onset temperature measured in accordance with ASTM E 2009 - 08 of at least 250 °C.

[0019] In some embodiments, the lubricating grease is a gel-like suspension of the unmodified natural thickening material in the oil base.

[0020] The inventors showed that a biodegradable lubricating grease having satisfactory lubricating properties can be prepared at room temperature using available natural resources, including a natural oil and a natural thickening material. Particularly, the inventors showed that there was no need for prior modification of the natural thickening material, by comparison to the known lubricating greases at least partly derived from natural resources. This is achieved by using a specific process *i.e.,* the ball milling. For this process, different suitable ball mills are available, including a tumbler ball mill, a planetary ball mill, a vibrational ball mill and an attritor-stirred ball mill. The use of a planetary ball mill is particularly suitable for preparing the lubricating grease of the present invention.

[0021] Ball milling is advantageous in that the collision between the balls at high energy mixes and grinds the materials together. It increases the uniformity of the mixing and allows the obtaining of a lubricating grease having superior dispersibility. Indeed, as the natural thickening material is getting mixed with the natural base oil, the ball collision also breaks the natural thickening material into smaller pieces up to the nanometer/micrometer level, thereby enhancing its dispersibility in the natural base oil. It is therefore obtained a lubricating grease having an improved dispersibility, without requiring the use of a solvent or without requiring chemical modification of the natural thickening material prior to mixing to increase its dispersibility.

[0022] Ball milling is also advantageous in that it is implemented for a short period of time and at room temperature, thereby avoiding the thermal degradation of the materials during the preparation and reducing the energy costs. It is obtained a lubricating grease having superior stability, thereby avoiding the incorporation of additives *e.g.*, antioxidants and preservatives, and being fully biodegradable, particularly in the absence of any chemical interactions (bonds) between the natural base oil and the natural thickening material.

[0023] The present invention makes it possible to address the needs expressed above. Particularly, the method and the lubricating grease of the present invention provide the following advantages:

- Provision of a biodegradable lubricating grease having satisfactory lubricating properties;
- Use of renewable sources for both the thickening material and the base oil;
- Provision of a lubricating grease having a simplified formulation;
- Provision of a simplified method for preparing the lubricating grease, particularly a method of reduced cost and time; and,
- Provision of a lubricating grease having satisfactory stability (for example no phase separation).

[0024] As mentioned above, the present invention provides a method for preparing a biodegradable lubricating grease at room temperature, without the need of modifying the natural thickening material. The biodegradable lubricating grease obtained still has satisfactory properties such as tribological properties, rheological properties, mechanical properties, physical properties and thermal properties, in comparison to conventional lubricating greases.

Brief description of the drawings

[0025]

Figure 1a illustrates the infrared (IR) spectra of lubricating greases.
Figure 1b illustrates the IR spectra of natural base oils.
Figure 2 illustrates the evolution of linear viscoelastic functions with the frequency of lubricating greases.
Figure 3 illustrates the evolution of linear viscoelastic functions with the frequency of lubricating greases.
Figure 4 illustrates the viscous flow curves of lubricating greases.
Figure 5 illustrates the viscous flow curves of lubricating greases.

Detailed description

[0026] The invention will now be described in more detail without limitation in the following description.

[0027] The term "*natural base oil*" as used herein refers to a naturally occurring fluid obtained from a biological source, such as a vegetable or animal source.

[0028] The term "*natural thickening material*" as used herein refers to a naturally occurring material obtained from a biological source, such as a vegetable or animal source, and having thickening properties. The natural thickening material may be an organic material, an inorganic material or a hybrid material.

[0029] The term "*unmodified thickening natural material*" as used herein refers to a natural thickening material, which has not been modified, particularly by implementing chemical reactions. The unmodified natural thickening material may have any suitable form *i.e.,* a raw material, a coarse material, an extract or a purified material.

[0030] The term "*biopolymeric material*" as used herein refers to any organic material comprising at least one natural polymer derived from a biological material. Typically, biopolymeric materials are produced by the cells of living organisms.

[0031] The term "*homogeneous dispersion*" as used herein refers to a system in which a material is distributed and dispersed uniformly in a continuous phase of another material, without any visible aggregation of the dispersed material.

[0032] The term "*functionalization*" as used herein refers to the addition of one or more chemical functional groups to a molecule.

[0033] The term "*ball mill*" as used herein refers to a closed system for grinding or blending materials, comprising a shell which rotates or oscillates about an axis, and which is partially filled with balls.

[0034] The term *"substantially free of*" as used herein means that the material comprises 1 % or less, preferably 0.1 % or less, more preferably 0.01 % or less, still more preferably about 0 % of a component.

[0035] The term *"room temperature*" as used herein means a temperature from 15 to 30°C, for example about 20°C.

[0036] The method of the present invention is carried out at atmospheric pressure unless otherwise specified.

[0037] All percentages are weight by weight of the lubricating grease, unless otherwise specified. All ratios or percentages are weight ratios or weight percentages unless specifically stated otherwise.

Lubricating grease

[0038] In one aspect, the present invention relates to a lubricating grease comprising at least one natural base oil, and at least one unmodified natural thickening material; wherein the lubricating grease has a penetration variation after working of from 0 to 20 dmm, a storage modulus G' value of from 10^1 to 10^7 Pa, and a loss modulus G" value lower than the G' value; and a friction coefficient at a load of 20N for 10 min of less than 0.1.

Natural base oil

[0039] The lubricating grease comprises at least one natural base oil.

[0040] The natural base oil may be selected from the group consisting of vegetable oil, animal oil, and combinations thereof; preferably the natural base oil is a vegetable oil.

[0041] The vegetable base oil may be selected from the group consisting of almond oil, babassu oil, camellia oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, groundnut oil, linseed oil, mustard oil, natural ester oil, olive oil, palm oil, peanut oil, rapeseed oil, rice bran oil, safflower oil, sesame oil, soybean oil, sunflower oil, tung oil, and combinations thereof; preferably from the group consisting of castor oil, rapeseed oil, colza oil, sunflower oil, and combinations thereof.

[0042] The animal oil may be selected from chrysalis oil, fish oil (*e.g.*, herring oil and sardine oil), lard, neatsfoot oil, tallow, turtle oil, and combinations thereof.

[0043] The natural base oil may be present in an amount by weight from 20 to 80 %, preferably from 30 to 70 %, more preferably from 30 to 60 %, with respect to the total weight of the mixture of the natural base oil and the unmodified natural thickening material.

Unmodified natural thickening material

[0044] The lubricating grease comprises at least one unmodified natural thickening material.

[0045] In some embodiments, the unmodified natural thickening material is an organic natural thickening material. In an alternative embodiment, the unmodified natural thickening material is an inorganic natural thickening material. In an alternative embodiment, the unmodified natural thickening material is a hybrid (organic and inorganic) natural thickening material.

[0046] The unmodified natural thickening material may be an unmodified thickening biopolymeric material; preferably the unmodified thickening biopolymeric material is obtained from the group consisting of bacteria, yeasts, fungi, plants, animals, and mixtures thereof; more preferably the unmodified thickening biopolymeric material is a biomass by-product; even more preferably the unmodified thickening biopolymeric material is a lignocellulosic material; still more preferably the lignocellulosic material is selected from the group consisting of barley straw, typha straw, rice straw, linen powder, and mixtures thereof.

[0047] The unmodified natural thickening material may comprise a biopolymer selected from the group consisting of cellulose, lignin, lignocellulose, hemicellulose, carboxymethyl cellulose, chitin, chitosan, polysaccharides, polyphenols, and mixtures thereof.

[0048] The unmodified natural thickening material may be a tannin-containing material, such as coffee grounds.

[0049] The unmodified natural thickening material may be selected from the group consisting of an eggshell, a crustacean waste (*e.g.*, shrimp shells or crab shells), insect exoskeletons, mushrooms, or human hair.

[0050] The unmodified natural thickening material may be present in an amount by weight from 20 to 80%, preferably from 30 to 70 %, more preferably from 40 to 70 % by total weight of the mixture of the natural base oil and the unmodified natural thickening material.

[0051] In some embodiments, the unmodified natural thickening material is not chemically modified; preferably the unmodified natural thickening material is not chemically modified by carbamidation, carboxymethylation, crosslinking, etherification, esterification, epoxidation, functionalization, phosphorylation, oxidation, and/or urethanization.

[0052] In some embodiments, the unmodified natural thickening material is not physically modified either, prior to mixing with the natural base oil, for example by a phenomenon of adsorption with another compound (different from the natural base oil).

[0053] In the lubricating grease, after dispersion into the natural base oil, the unmodified natural thickening material may have any suitable form; for example a spherical form, an ellipsoidal form, an elongated form, a cylindrical form, an oval form, a polygonal form, a dendritic (tree-like) form, or a beads-on-a-string form. The form of the unmodified natural thickening material in its dispersed state may depend on the type of thickening material and the conditions for preparing the lubricating grease.

[0054] In some embodiments, the unmodified natural thickening material has a particle size from 0.01 to 50 μm, preferably a particle size from 0.1 to 30 μm. The particle size may be measured visually by observation with a scanning electron microscope (SEM).

[0055] The particle size may be the mean thickness for the cylindrical form or the elongated form. The "*thickness*" for the cylindrical form refers to, in a cross-section cut perpendicularly to the length direction (direction of the length along the longest axis), a diameter or a major axis of the cross-section. The "*thickness*" for the elongated form refers to, in a cross-section cut perpendicularly to the length direction, a diameter of the circumcircle of the cross-section.

[0056] The particle size may be the mean diameter of the circumcircle for the polygonal form.

[0057] The particle size may be the mean diameter of the mean diameter or mean major axis of the spherical forms or the oval forms (corresponding to "*beads*" of the beads-on-a-string form) for the beads-on-a-string form.

Additives and other ingredients

[0058] In some embodiments, the lubricating grease may comprise at least one additive; preferably the additive may be selected from the group consisting of a rust inhibitor, an antioxidant, a lubricity improver, a dispersing auxiliary agent, a detergent, a corrosion inhibitor, a defoaming agent, an extreme pressure agent, a metal deactivator, and a combination thereof.

[0059] If present, the lubricating grease comprises less than 5 %, preferably less than 3 %, more preferably less than 1 %, of the additive(s), with respect to the total weight of the mixture of the natural base oil and the unmodified natural thickening material.

[0060] In an alternative embodiment, the lubricating grease may be substantially free of additives.

[0061] In another embodiment, the lubricating grease is substantially free of mineral oil.

[0062] In another embodiment, the lubricating grease is substantially free of a solvent.

[0063] In another embodiment, the lubricating grease consists of at least one natural base oil and at least one unmodified natural thickening material.

Properties of the lubricating grease

[0064] The lubricating grease preferably is a homogeneous dispersion with suitable physical and mechanical stability, and rheological and tribological properties.

[0065] Particularly, the lubricating grease may show adequate anti-friction and anti-wear properties.

[0066] The lubricating grease advantageously shows no phase separation during the product shelf life, thereby confirming satisfactory stability.

[0067] The interaction between the natural base oil and the unmodified natural thickening material in the lubricating grease substantially is only physical. In other words, there is substantially no chemical interaction between the natural base oil and the unmodified natural thickening material in the lubricating grease, such as crosslinking.

[0068] The absence of a chemical interaction between the natural base oil and the unmodified natural thickening material is advantageous in that the natural base oil and the unmodified natural thickening material are more easily separable when treating used lubricating greases and that it increases the biodegradability of the lubricating grease.

[0069] The lubricating grease preferably is a gel-like suspension of the unmodified natural thickening material in the natural base oil. The term "*gel-like*" as used herein refers to a gel or to any composition having physical properties (*e.g.*, viscosity, elasticity) characteristic of a gel.

[0070] The onset temperature at which the thermal decomposition of the lubricating grease begins may be 250°C or higher, preferably 300°C or higher, and more preferably 320°C or higher. The onset temperature may be obtained by a conventional thermogravimetric analysis from room temperature to 900°C at a heating rate of 10°C/min.

[0071] The lubricating grease may have a friction coefficient less than 0.2, or less than 0.15, preferably less than 0.1. The friction coefficient may be obtained using a conventional rheometer, specifically by applying a constant normal load of 20 N for 10 min.

[0072] The lubricating grease may have a negligible penetration variation, for example, 80 dmm (decimilimeter) or less, 70 dmm or less, 60 dmm or less; and or preferably 50 dmm or less. The penetration variation refers to the difference between the unworked penetration (dmm) and the worked penetration (dmm). The unworked and worked penetration may be measured using a 1/4-scale cone equipment and following ASTM D 1403-83 standard. The results may be converted to the standard penetration (equivalent full-scale cone penetration values) according to the equation established on the standard.

[0073] The lubricating grease may have a NLGI (National Lubricating Grease Institute) consistency number from 000 to 6, or 000 to 3, or 000 to 1, depending on the raw material and concentration used. The NLGI consistency number (also called "NLGI grade") measures the relative hardness of a grease used for lubrication, as specified by the standard classification of lubricating grease established by the NLGI. The NLGI grade may be calculated from the above penetration values according to ASTM D 217.

[0074] The lubricating grease may provide a wear mark of less than 400 μm in diameter, preferably less than 300 μm in diameter, and more preferably less than 200 μm in diameter, or less than 300 μm in diameter. The wear mark may be obtained from the measurement of the friction coefficients as explained above (i.e., wear marks on the steel plates of the rheometer resulting from a load of 20N for 10 min) and its diameter may be measured using optical microscopy.

[0075] The lubricating grease may have an oxidation onset temperature of at least 250°C, or at least 260°C, or at least 280°C, or at least 300°C. The oxidation onset temperature may be measured according to the ASTM E2009-08 standard.

Method for preparing lubricating grease

[0076] In another aspect, the present invention relates to a method for preparing a lubricating grease.

[0077] The method of the present invention comprises the following steps:

a) providing at least one natural base oil;
b) providing at least one unmodified natural thickening material;
c) ball milling the at least one natural base oil and the at least one unmodified natural thickening material for obtaining a lubricating grease.

[0078] The ball milling is carried out using a ball mill; preferably a ball mill selected from the group consisting of a tumbler ball mill, a planetary ball mill, a vibrational ball mill and an attritor-stirred ball mill; more preferably wherein the ball mill is a planetary ball mill.

[0079] The ball mill may contain a hollow shell (also referred to as a bowl) which is partially filled with balls (e.g., from 1 to 100 balls).

[0080] A tumbler ball mill corresponds to a cylindrical mill which usually rotates around a horizontal axis. A tumbler ball mill is commercially available under the name of, for instance, MQG0909 from YanTai JinPeng Mining Machinery Co., Ltd.

[0081] A planetary ball mill corresponds to a cylindrical mill which rotates in a planetary movement around, usually, a vertical axis. A planetary ball mill is commercially available under the name of, for instance, PM100 from Retsch®.

[0082] A vibrational ball mill is usually a cylindrical mill which oscillates, or vibrates, centered on a single point, usually horizontally. A vibrational ball mill is commercially available under the name of, for instance MM 500 from Retsch®.

[0083] An attritor-stirred ball mill corresponds to a rotational mill which also includes internal agitation within the mill. An attritor-stirred ball mill is commercially available under the name of, for instance, 010E-500 from Sepor Inc.

[0084] The shell may be made of, for example, stainless steel, agate, zirconia, or tungsten carbide, ceramic, and the balls may be made of the same material as the shell, having variable diameters.

[0085] Thanks to the energy applied by the high-energy collisions of the balls inside the shell, the unmodified natural thickening material is grinded in smaller pieces up to the nanometer/micrometer level.

[0086] Thus, the present invention makes it possible to grind and homogeneously and uniformly mix the unmodified natural thickening material with the natural base oil, resulting in consistency, texture and properties that cannot be obtained using conventional mixing techniques (*e.g.*, using a common agitator such as an anchor or an helicoidal stirrer, a triple-roll mill, a rotor-stator colloidal mill, a high-pressure homogenizer, etc.) at room or high temperature.

[0087] The natural base oil, the unmodified natural thickening material, and the lubricating grease are as defined above.

[0088] The unmodified natural thickening material may be provided as a coarse material. The term "*coarse material*" as used herein means that the provided unmodified natural thickening material has a structure lacking in fineness, or a structure composed of large parts. By contrast, in the resulting lubricating grease *i.e.,* after performing step (c), the natural thickening material is broken into smaller pieces up to the nanometer/micrometer level, thereby enhancing its dispersibility in the natural base oil.

[0089] The unmodified natural thickening material may be provided in any suitable form, for example as a raw material, as an extract or as a purified material.

[0090] The unmodified natural thickening material may be provided as an unprocessed material (*e.g.*, not cleaned, not dried, not frozen, not sliced, not liquefied and/or not dissolved), which is therefore used as it is after being harvested/collected, or as a processed material (*e.g.*, cleaned, dried, frozen, sliced, liquefied, dissolved, extracted and/or purified).

[0091] The natural base oil and the unmodified natural thickening material may be provided in a weight ratio from 8:2 to 2:8, preferably from 7:3 to 3:7, more preferably from 4:6 to 6:4.

[0092] In some embodiments, the natural base oil and the unmodified natural thickening material are unheated (not heated) prior to carrying out the ball milling step.

[0093] Preferably, in the method of the invention, the natural base oil and the unmodified natural thickening material may be ball milled at room temperature; preferably at a temperature from 15 to 30 °C; for example, at about 20 °C.

[0094] The ball mill step may be carried out for a time period from 1 min to 24 h, preferably from 5 min to 10 h, more preferably from 5 min to 5 h, still more preferably from 5 min to 2 h, most preferably from 15 to 60 min.

[0095] The ball mill step may be carried out at a rotation speed from 50 to 2000 rpm, preferably from 100 to 1500 rpm, more preferably from 300 to 1500 rpm, most preferably from 500 to 1500 rpm.

[0096] The ball mill step may be carried out at a frequency from 5 to 1000 Hz, preferably from 10 to 100 Hz.

[0097] In some embodiments, no mineral oil is provided in addition to the natural base oil. The lubricating grease obtained thereof is therefore substantially free of mineral oil.

[0098] In some embodiments, no solvent is provided. Solvents are usually used in order to increase the dispersibility of the thickening material. The use of a ball mill therefore avoids using such solvent, as the dispersibility of the unmodified natural thickening material is increased by a mechanical action *i.e.*, by the collision at high energy of the balls.

[0099] The method of the present invention may further comprise a step of recovering the resulting lubricating grease.

[0100] In another aspect, the present invention relates to the lubricating grease obtained by the method as defined above.

Examples

[0101] The following examples illustrate the lubricating grease according to the present disclosure. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present disclosure.

[0102] Unless otherwise specified, the equipment and ball milling protocol used in Example 1 are used in all the

Examples.

Example 1: IR spectroscopy

Lubricating greases

[0103]

Formulation 1: 55% of lignin and 45% of castor oil
Formulation 2: 50% of lignin and 50% of colza oil.

Equipment

[0104] A stainless-steel ball mill having a 250-mL capacity (internal diameter: 62 mm) and containing 50 balls (diameter: 10 mm) is used.

Ball milling protocol

[0105]

Duration: 30 min
Temperature: room temperature
Rotation speed: 500 rpm.

IR methodology

[0106] The IR spectra of formulations 1 and 2 are obtained according to the conventional procedure, in a wavenumber range of 600 to 4000 cm^{-1} in the transmission mode.

Figures

[0107] The results are shown in Figure 1a. The y-axis and x-axis refer to the transmittance and wavenumber (cm^{-1}). The IR spectrum in black corresponds to formulation 1, and the IR spectrum in gray corresponds to formulation 2. For comparison, the IR spectra of colza oil (black) and castor oil (grey) alone are shown in Figure 1b.

Results

[0108] No new peak is observed in the IR spectra of formulations 1 and 2 compared to the IR spectra of the colza oil and castor oil alone. Likewise, no new peak is observed in the IR spectra of formulations 1 and 2 compared to the IR spectrum of lignin alone (not shown). This indicates that formulations 1 and 2 have undergone no chemical changes during the preparation, and thus, the interaction between the natural base oil (castor oil or colza oil) and the unmodified natural thickening material (lignin) is not chemical but physical.

[0109] The absence of any chemical interaction between the natural base oil and the unmodified natural thickening material is advantageous in that the method is versatile in terms of the materials to be used (the natural base oil and the unmodified natural thickening material). Since the chemical structure of the materials to be used does not matter for the formation of a homogenous dispersion, any combination of any natural base oil and any unmodified natural thickening material may be used.

Example 2: Small-amplitude oscillatory shear tests

Lubricating greases

[0110]

Formulation 3: 30% of lignin and 70% of castor oil
Formulation 4: 40% of lignin and 60% of castor oil
Formulation 5: 50% of lignin and 50% of castor oil
Formulation 6: 55% of lignin and 45% of castor oil

Formulation 7: 60% of lignin and 40% of castor oil
Formulation 8: 70% of lignin and 30% of castor oil
Formulation 9: 40% of Typha straw and 60% of castor oil
Formulation 10: 60% of Barley straw and 40% of castor oil
Formulation 11: 30% of Barley straw and 70% of castor oil
Formulation 12: 40% of linen powder and 60% of castor oil
Formulation 13: 40% of rice straw and 60% of castor oil

Methodology for small-amplitude oscillatory shear test

[0111] The linear viscoelastic functions (storage G' and loss G" moduli) of formulations 3 to 13 in the range of 0.03 to 100 rad/s are measured with rough plate-plate geometries using a controlled-stress rheometer.

[0112] The storage modulus G' represents the elastic component of a material and relates to the material's ability to store energy elastically while the loss modulus G" represents the viscous component of a material and relates to the material's ability to dissipate stress. These parameters are often used to characterize viscoelastic materials, which show both viscous and elastic behaviors, such as a grease.

Figures

[0113] The results are shown in figure 2 and figure 3, in which the y-axis corresponds to the values of the storage modulus G' (Pa, open symbols) and the loss modulus G" (Pa, closed symbols), and the x-axis corresponds to the angular frequency ω (rad/s) of the rheometer. The signification of symbols is as follows.

Figure 2

[0114]

Squares (open for G' and closed for G"): formulation 3;
Circles (open for G' and closed for G"): formulation 4;
Up triangles (open for G' and closed for G"): formulation 5;
Left triangles (open for G' and closed for G"): formulation 6;
Down triangles (open for G' and closed for G"): formulation 7; and
Diamonds (open for G' and closed for G"): formulation 8.

Figure 3

[0115]

Squares (open for G' and closed for G"): formulation 9;
Circles (open for G' and closed for G"): formulation 10;
Down triangles (open for G' and closed for G"): formulation 11;
Diamonds (open for G' and closed for G"): formulation 12; and
Up triangles (open for G' and closed for G"): formulation 13.

Results

[0116] As seen from figure 2 and figure 3, G" values are lower than G' values, which is a typical behavior observed in commercial lubricating greases.

[0117] Thus, these results indicate that the above formulations have similar rheological behavior to the commercial lubricating greases, and thus have satisfactory lubricating properties.

Example 3: Viscous flow measurements

Lubricating greases

[0118] Formulations 3 to 8 and formulations 9, 11, 12 and 13 are used for viscous flow measurements.

Viscous flow measurement methodology

[0119] The evolution of the viscosity of each formulation is evaluated as a function of the shear rate in the range of 0.01 to 100 s^{-1}, using the rough plate-plate geometry with the controlled-strain rheometer, as in example 2.

Figures

[0120] The results are shown in figure 4 and figure 5, in which the y-axis corresponds to the viscosity η (Pa s) and the x-axis corresponds to the shear rate (s^{-1}). The signification of symbols is as described in example 2. The hexagon in figure 4 represents castor oil alone for comparison.

Results

[0121] As shown in figure 4 and figure 5, most of the formulations show shear thinning behavior, which is typical of commercial lubricating greases. A stronger tendency to shear thinning is observed in formulations with relatively higher lignin content (such as 60% and 70% compared to 30% and 40%, see figure 4). Likewise, for formulations from straws, a stronger tendency to shear thinning is observed in formulations with higher straw content (40% compared to 30%, see figure 5). In all cases, the addition of lignin/straw resulted in an increased viscosity of the castor oil.

[0122] Thus, the present invention provides biodegradable lubricating greases having satisfactory viscous flow properties.

Example 4: Mechanical stability

Lubricating greases

[0123]

Formulation 6: as in example 2
Formulation 14: 60% of lignin and 40% of rapeseed oil

Methodology for mechanical stability

[0124] The mechanical stability of formulations 6 and 14 is evaluated by the roll stability test in accordance with ASTM D 1831. The unworked and worked penetration are evaluated by using 1/4-scale cone equipment in accordance with ASTM D 1403 - 83 standard. The results are converted to the standard penetration (equivalent full-scale cone penetration values) according to the equation established on the standard, and the NLGI grades are calculated from the above penetration values according to ASTM D 217.

Results

[0125] The results are shown in Table 1. For comparison, the results of commercial lubricating greases, lithium-based grease and calcium-based grease, obtained from R. Sánchez et.al., 2014, Tribol. Trans., 57:3, 445-454, are also shown.

Table 1. Unworked and worked penetration, and NLGI grade (Legend: dmm = decimilimeter (mm/10 | Lithium LG = lithium-based grease | Calcium LG = calcium-based grease)

Sample	Unworked penetration (dmm)	Worked penetration (dmm)	Penetration variation (dmm)	NLGI grade
Lithium LG	260	253	-7	2-3
Calcium LG	279	373	94	2
Formulation 6	583	572	-11	000
Formulation 14	436	395	-41	00

[0126] The results presented in Table 1 show that the mechanical stability is preserved in the lubricating greases after performing the roll stability test.

Example 5: Thermal stability

Lubricating greases

[0127] Formulations 3 and 7: as in example 2

Methodology for thermal stability

[0128] The thermal stability of formulations 3 and 7 is evaluated by thermogravimetric analysis from room temperature to 900°C at a heating rate of 10 °C/min.

Results

[0129] The results are shown in Table 2. For comparison, the results of commercial lubricating greases, lithium-based grease and calcium-based grease, obtained from the above-mentioned R. Sánchez et.al., are also shown.

Table 2: Thermogravimetric Analysis (TGA) (Legend: Lithium LG = lithium-based grease | Calcium LG = calcium-based grease)

Sample	T_{onset}	T_{max}	T_{final}	ΔW (%)	Residue (%)
Lithium LG	286	359/453	468	97	3
Calcium LG	325	362/456	476	94	6
Formulation 3	345	374	418	87	13
Formulation 7	327	364	418	72	28

[0130] In Table 2, the temperature for the onset of thermal decomposition (T_{onset}), the temperature at which decomposition rate is maximum (T_{max}), the temperature at which the thermal event ends (T_{final}), the loss weight at the end of each decomposition step (ΔW (%)) and the percentage of non-degraded residue (Residue (%)) have been estimated from the thermograms of the samples.

[0131] As clear from the results in Table 2, formulations 3 and 7 show better thermal stability than the commercial lubricating greases.

Example 6: Tribological behavior and anti-wear property

Lubricating greases

[0132]

Formulation 5 to 7, 9, 10, 11 and 14: as in example 2
Formulation 15: 60% of lignin and 40% of sunflower oil

Methodology for tribological behavior

[0133] The friction coefficients of each formulation are obtained using a conventional rheometer, specifically by applying a constant normal load of 20 N and setting a constant rotational speed of 10 rpm for 10 min. The results are obtained as the average of four tests.

Results

[0134] The results are shown in **Table 3**. For comparison, the results of commercial lubricating greases, lithium-based grease and calcium-based grease, obtained from Borrero-López et al. 2018., J. Renew. Mater., 6(4), 347-361, are also shown.

Table 3: Friction coefficient (Legend: Lithium LG = lithium-based grease | Calcium LG = calcium-based grease)

Sample	Friction coefficient
Lithium LG	0.108
Calcium LG	0.107
Formulation 5	0.034
Formulation 6	0.045
Formulation 7	0.063
Formulation 9	0.120
Formulation 10	0.120
Formulation 11	0.120
Formulation 14	0.063
Formulation 15	0.047

[0135] Table 3 demonstrates that reasonably low friction coefficient values are obtained for the tested formulations. Importantly, lignin-based lubricating greases (formulations 5 to 7, 14 and 15) have extremely low values, and thus resulted in a better friction coefficient than the commercial lubricating greases.

<u>Methodology for anti-wear property</u>

[0136] The wear marks formed in the steel plates of the tribology measuring cell coupled with the rheometer used for the measurement of friction coefficients are evaluated by measuring the diameter, using optical microscopy.

<u>Results</u>

[0137] The results are shown in Table 4. For comparison, the results of commercial lubricating greases, lithium-based grease and calcium-based grease, adapted from the above-mentioned R. Gallego, et.al. (2016) are also shown.

Table 4: Diameter of wear marks obtained by friction (Legend: Lithium LG = lithium-based grease | Calcium LG = calcium-based grease)

Sample	Wear mark diameter (μm)
Lithium LG	218
Calcium LG	257
Formulation 5	0
Formulation 6	130
Formulation 7	196
Formulation 14	160
Formulation 15	116

[0138] As seen from Table 4, the size of the wear marks is significantly reduced for the lubricating greases of the invention as compared to the commercial lubricating greases, highlighting the anti-wear properties of lignocellulose and vegetable oils.

Example 7: Oxidation onset temperature

<u>Lubricating greases</u>

[0139]

Formulations 6 and 10: as in example 2
Formulation 16: 60% of lignin and 40% of colza oil

Methodology for oxidation onset temperature

[0140] The oxidation resistance of each formulation is evaluated by measuring the oxidation onset temperature according to ASTM E2009-08 standard. The results are shown in Table 5.

[0141] For comparison, the results of commercial lubricating greases, lithium-based grease, calcium-based grease and cellulose nanofiber-based grease, adapted from Lube-tech, 2014, Lube Magazine No.122(94), 1-6, and Claudia Roman et al., 2021; J. Clean. Prod, 319, 128673, are also shown.

Table 5: Oxidation onset temperature (Legend: Lithium LG = lithium-based grease | Calcium LG = calcium-based grease)

Sample	Oxidation onset temperature (°C)
Lithium LG	207
Calcium LG	236
Cellulose nanofiber-based LG	190-214
Formulation 6	343
Formulation 10	334
Formulation 15	287

[0142] Results of Table 5 show that the lubricating greases of the present invention have a higher oxidation onset temperature, thus better oxidation resistance than the commercial lubricating greases.

Claims

1. A method for preparing a lubricating grease, wherein the method comprises the following steps:

   a) providing at least one natural base oil;
   b) providing at least one unmodified natural thickening material;
   c) ball milling the at least one natural base oil and the at least one unmodified natural thickening material for obtaining a lubricating grease.

2. The method according to claim 1, wherein the step of ball milling is carried out using a ball mill; preferably a ball mill selected from the group consisting of a tumbler ball mill, a planetary ball mill, a vibrational ball mill and an attritor-stirred ball mill; preferably wherein the ball mill is a planetary ball mill.

3. The method according to any of the preceding claims, wherein the natural base oil is selected from the group consisting of vegetable oil, animal oil, and combinations thereof; preferably wherein the at least one natural base oil is a vegetable base oil; more preferably wherein the vegetable base oil is selected from the group consisting of almond oil, babassu oil, camellia oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, groundnut oil, linseed oil, mustard oil, olive oil, palm oil, peanut oil, rapeseed oil, rice bran oil, safflower oil, sesame oil, soybean oil, sunflower oil, tung oil, and combinations thereof.

4. The method according to any of the preceding claims, wherein the at least one unmodified natural thickening material is obtained from the group consisting of bacteria, yeasts, fungi, plants, animals, and mixtures thereof; preferably the unmodified natural thickening material is a biomass by-product; more preferably the unmodified natural thickening material is a lignocellulosic material; still more preferably the lignocellulosic material is selected from the group consisting of barley straw, typha straw, rice straw, linen powder, and mixtures thereof.

5. The method according to any of the preceding claims, wherein the at least one unmodified natural thickening material is a raw material or a purified material.

6. The method according to any of the preceding claims, wherein the at least one unmodified natural thickening material is not chemically modified; preferably wherein the unmodified natural thickening material is not chemically modified by carbamidation, carboxymethylation, crosslinking, etherification, esterification, epoxidation, functionalization, phosphorylation, oxidation, urethanization.

7. The method according to any of the preceding claims, wherein the at least one natural base oil and the at least one unmodified natural thickening material are provided in a weight ratio of from 8:2 to 2:8.

8. The method according to any of the preceding claims, wherein no solvent is provided.

9. A lubricating grease obtained by the method according to any preceding claims.

10. A lubricating grease comprising:

a) at least one natural base oil; and
b) at least one unmodified natural thickening material;
wherein the lubricating grease has a penetration variation after working of from 0 to 20 dmm, a storage modulus G' value of from 10^1 to 10^7 Pa, and a loss modulus G" value lower than the G' value; and a friction coefficient at a load of 20N for 10 min of less than 0.1.

11. The lubricating grease according to claim 10, wherein the lubricating grease provides a wear mark resulting from a load of 20N for 10 min of less than 400 μm in diameter.

12. The lubricating grease according to claim 10 or 11, wherein the lubricating grease comprises from 20 to 80 %, preferably from 30 to 60 %, of the at least one unmodified natural thickening material, by total weight of the mixture of the natural base oil and the unmodified natural thickening material.

13. The lubricating grease according to any one of claims 10 to 12, wherein the lubricating grease has an oxidation onset temperature measured in accordance with ASTM E 2009 - 08 of at least 250 °C.

14. The lubricating grease according to any one of claims 10 to 13, wherein the lubricating grease is a gel-like suspension of the unmodified natural thickening material in the natural oil base.

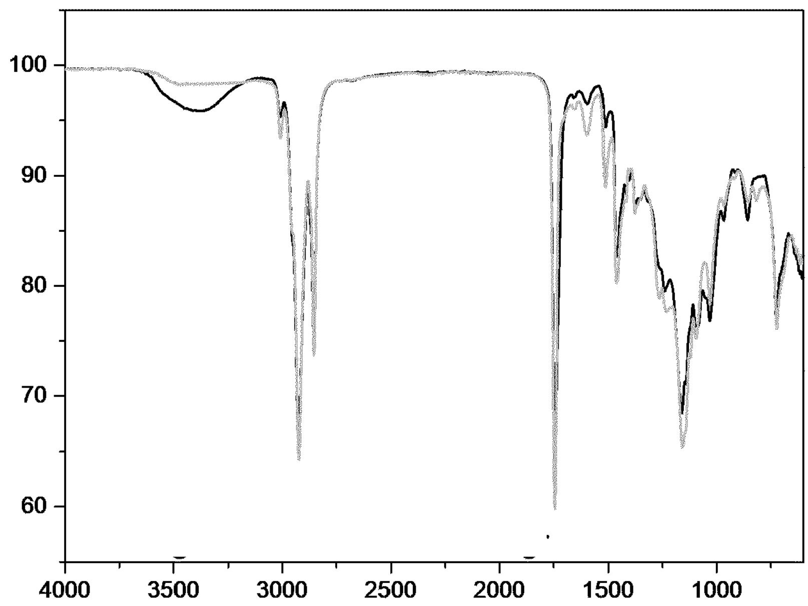

Figure 1a

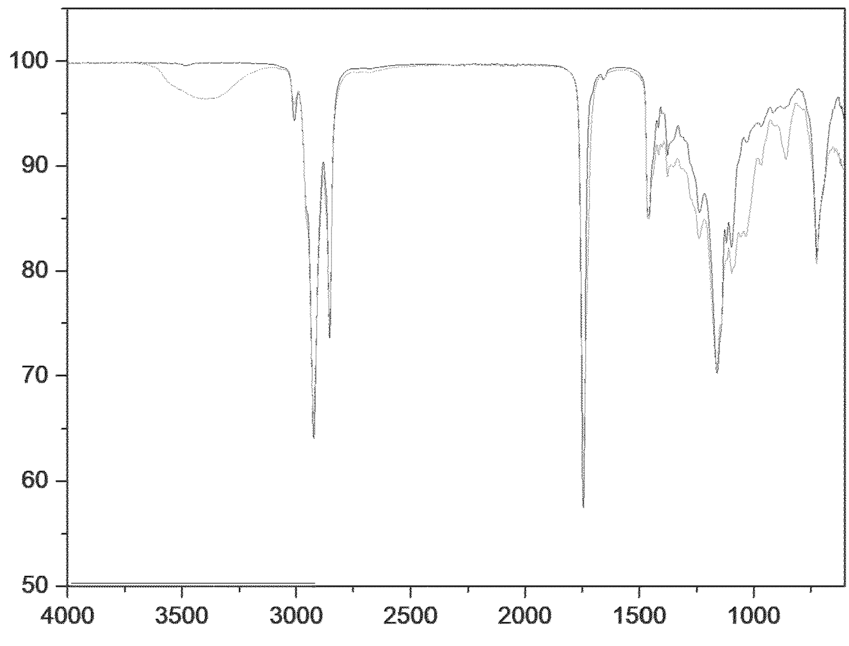

Figure 1b

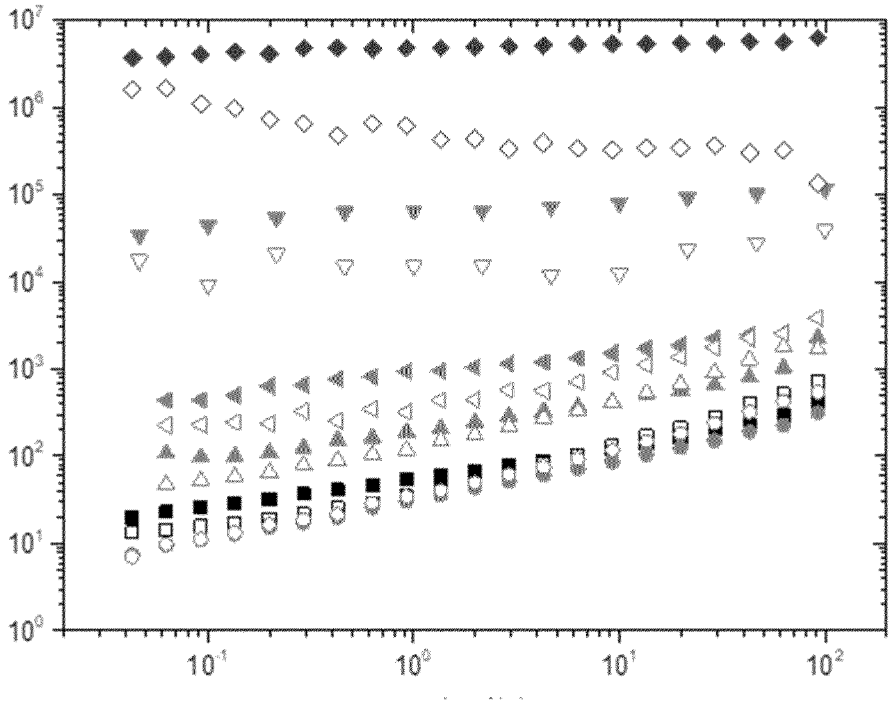

Figure 2

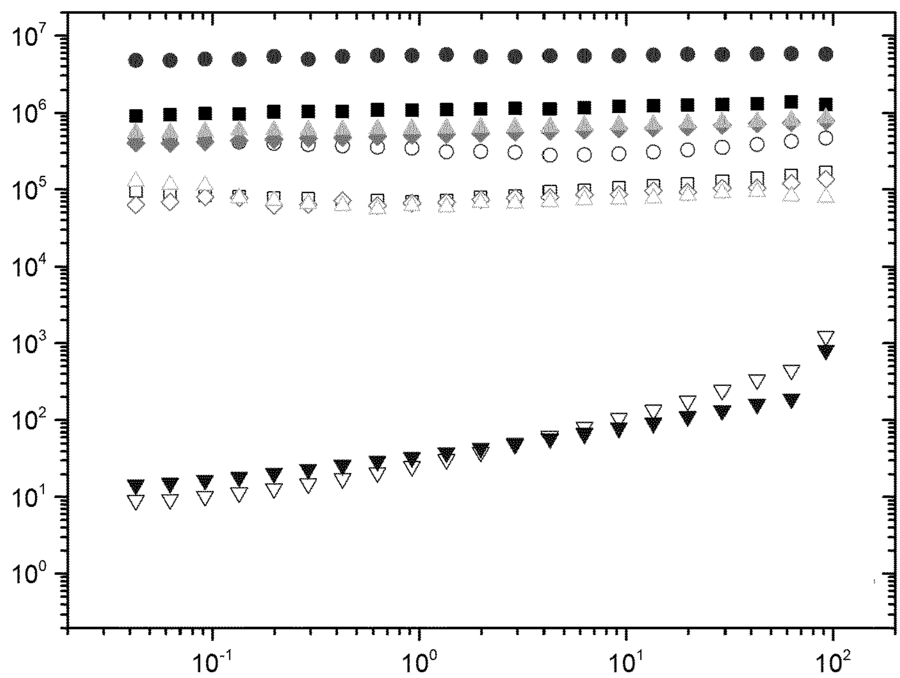

Figure 3

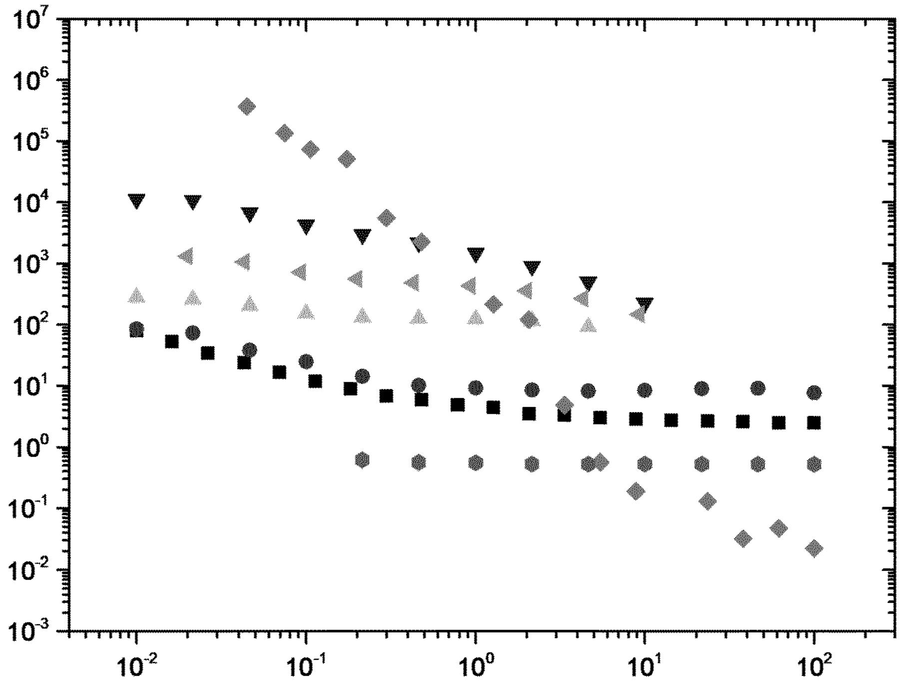

Figure 4

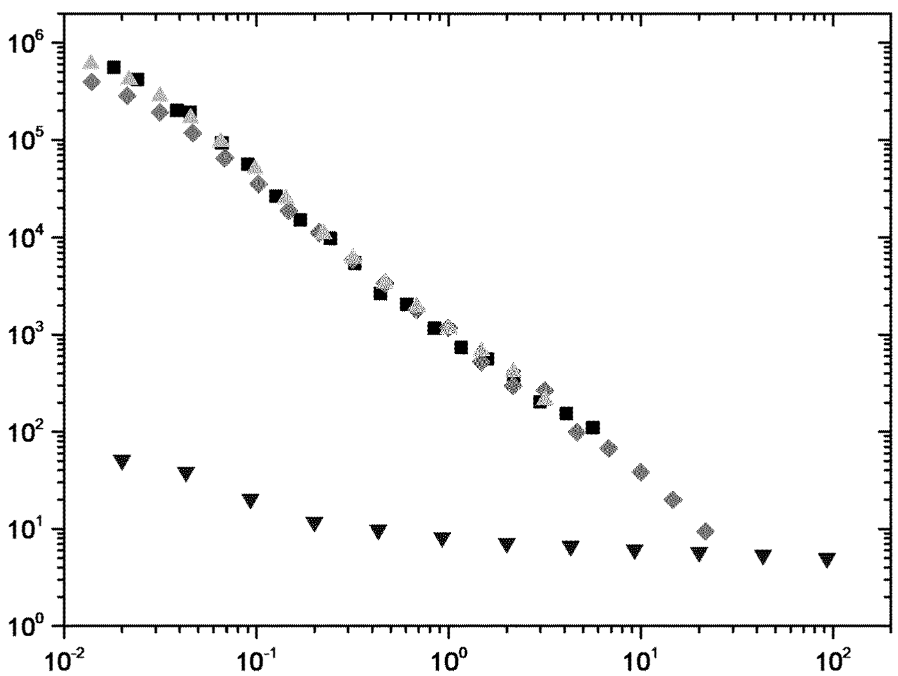

Figure 5

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PARTIAL EUROPEAN SEARCH REPORT

under Rule 62a and/or 63 of the European Patent Convention. This report shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 23 15 5679

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 A	US 2013/338049 A1 (KING JAMES [US] ET AL) 19 December 2013 (2013-12-19) * claims 1, 11; par. 21, 2, 6, 27 *	10-14 1-9	INV. C10M169/02 ADD. C10N30/02 C10N30/06 C10N30/08 C10N30/10 C10N30/00 C10N50/10 C10N70/00
X	WO 2017/200098 A1 (NTN TOYO BEARING CO LTD [JP]; HATTORI SHOTEN CO LTD [JP]) 23 November 2017 (2017-11-23) * paragraphs [0023], [0038]; claims 1, 2, 4 *	10,11, 13,14	
X	ACAR NAZLI ET AL: "Tribological and Rheological Characterization of New Completely Biogenic Lubricating Greases: A Comparative Experimental Investigation", LUBRICANTS, vol. 6, no. 2, 5 May 2018 (2018-05-05), page 45, XP093095080, DOI: 10.3390/lubricants6020045 * table 1 *	10,11, 13,14	
X	CN 112 680 269 A (CHINA RAILWAY NO 10 ENG GROUP CO LTD ET AL.) 20 April 2021 (2021-04-20) * claims 1-2 *	10-14	TECHNICAL FIELDS SEARCHED (IPC) C10M C10N

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC so that only a partial search (R.62a, 63) has been carried out.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

1

Place of search	Date of completion of the search	Examiner
Munich	25 October 2023	Greß, Tobias

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

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INCOMPLETE SEARCH SHEET C

Application Number
EP 23 15 5679

Claim(s) completely searchable:
-

Claim(s) searched incompletely:
1-14

Reason for the limitation of the search:

Present claims 1-14 relate to an extremely large number of possible methods and products. Support and disclosure within the meaning of Articles 84 and 83 EPC are to be found, however, for only a very small proportion of the methods and products claimed, i.e.
a method for preparing a lubricating grease and a lubricating grease obtained by the method, wherein the method comprises
the following steps:
a) providing at least one natural base oil being a naturally occurring fluid
obtained from a biological source;
b) providing at least one unmodified natural thickening material being a naturally occurring material obtained from a biological source, wherein the at least one unmodified natural thickening material is not chemically modified;
c) ball milling the at least one natural base oil and the at least one unmodified natural thickening material for obtaining a lubricating grease,
wherein the at least one natural base oil is selected from the group consisting of vegetable base oil, animal oil, and combinations thereof, and
wherein the at least one unmodified natural thickening material is a selected from the group consisting of lignin, lignocellulose, and mixtures thereof (cf. p. 5, l. 5-9; claims 3-4, 6; p. 7, l. 3-6; examples).
Non-compliance with the substantive provisions is such that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 63 EPC and Guidelines B-VIII, 3).

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

EP 23 15 5679

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
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25-10-2023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013338049 A1	19-12-2013	NONE	
WO 2017200098 A1	23-11-2017	NONE	
CN 112680269 A	20-04-2021	NONE	

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2019127532 A **[0003]**
- EP 3677662 A1 **[0004]**
- EP 3290497 A1 **[0004]**
- JP 2013116991 A **[0004]**

Non-patent literature cited in the description

- **R. GALLEGO.** *ACS Sustainable Chem. Eng.,* 2015, vol. 3 (9), 2130-2141 **[0004]**
- **R. GALLEGO et al.** *Tribol. Int.,* 2016, vol. 94, 652-660 **[0004]**
- **ANTONIO M. BORRERO-LÓPEZ et al.** *ACS Sustainable Chem. Eng.,* 2018, vol. 6 (4), 5198-5205 **[0004]**
- **R. SÁNCHEZ.** *Tribol. Trans.,* 2014, vol. 57 (3), 445-454 **[0125]**
- **BORRERO-LÓPEZ et al.** *J. Renew. Mater.,* 2018, vol. 6 (4), 347-361 **[0134]**
- **LUBE-TECH.** *Lube Magazine,* 2014, vol. 122 (94), 1-6 **[0141]**
- **CLAUDIA ROMAN et al.** *J. Clean. Prod,* 2021, vol. 319, 128673 **[0141]**