(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 428 250 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
16.01.2019 Bulletin 2019/03

(51) Int Cl.:
C10M 123/04 *(2006.01)*

(21) Application number: **17180781.1**

(22) Date of filing: **11.07.2017**

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

(71) Applicant: **Shell Internationale Research Maatschappij B.V.**
2596 HR The Hague (NL)

(72) Inventors:
- **WORTHINGTON, Edward Alexander**
  21107 Hamburg (DE)
- **WHEATLEY, Alan Richard**
  London SE 7NA (GB)
- **EGGENSTEIN, Matthias**
  21107 Hamburg (DE)
- **HE, Qiwei**
  Belle Mead, NJ 08502 (US)
- **THOMPSON, Donovan Lamar**
  Franklin Park, NJ 08823 (US)
- **LEBLANC, Jean-Pierre**
  Hillsborough, NJ 08844 (US)
- **WILLIAMS, Neal St. John**
  Berkshire RG42 3JN (GB)

(74) Representative: **Shell Legal Services IP**
p/a Carel van Bylandtlaan 16
2596 HR Den Haag (NL)

(54) **GREASE AND PROCESS FOR PREPARING A GREASE**

(57) A grease comprising:
(a) greater than 60wt% of a base oil;
(b) from 1 to 19wt% of a metal soap; and
(c) from 1 to 19wt% of a dispersing polymer,
wherein the weight percentages are based upon the weight of the grease.
The incorporation of a dispersing polymer enables the skilled person to incorporate less metal soap yet still provide a grease with desirable properties.

EP 3 428 250 A1

Description

Field of the Invention

[0001] The invention relates to a lubricating grease and to a process for preparing a lubricating grease.

Background of the Invention

[0002] Greases are used to provide lubrication in a variety of applications including bearings for constant-velocity joints, ball joints, wheel bearings, alternators, cooling fans, ball screws, linear guides of machine tools, sliding areas of construction equipment, and bearings and gears in steel equipment and various other industrial mechanical facilities.

[0003] Greases thickened with lithium soaps account for around 80% of global grease production. It is desirable to develop greases containing no lithium or less lithium because the cost of lithium is increasing as more lithium is used in lithium ion batteries.

[0004] The present inventors have sought to provide a grease that has comparable properties to current lithium-based greases, but contains a reduced amount of lithium. The present inventors have also sought to provide a process for the manufacture of such greases.

Summary of the Invention

[0005] Accordingly, the invention provides a grease comprising:

(a) greater than 60wt% of a base oil;
(b) from 1 to 19wt% of a metal soap; and
(c) from 1 to 19wt% of a dispersing polymer,

wherein the weight percentages are based upon the weight of the grease.

[0006] The inventors have surprisingly found that incorporating a dispersing polymer enables the skilled person to incorporate less metal soap yet still provide a grease with desirable properties.

Detailed Description of the Invention

[0007] The grease comprises greater than 60wt% of a base oil, wherein the weight percentage is based upon the weight of the grease. Preferably the grease comprises greater than 70wt% of a base oil, more preferably greater than 80wt%. Preferably the grease comprises less than 95wt% of a base oil, more preferably less than 92wt%.

[0008] The base oil is one which may ordinarily be used as the base oil of a grease composition and there are no special restrictions. The base oil is suitably chosen from mineral oils, synthetic oils, synthetic esters, naphthenic oils or animal and plant oils, and mixtures thereof.

[0009] In particular, it is possible to use, singly or as mixtures, base oils which belong to Group I, Group II, Group III, Group IV, Group V and so on of the API (American Petroleum Institute) base oil categories. Preferably the grease comprises base oils which belong to Group I or Group II of the API base oil categories, and more preferably the base oil consists essentially of one or more Group I or Group II base oils or group V Naphthenic base oils.

[0010] Group I base oils include, for example, paraffinic mineral oils obtained by a suitable combination of refining processes such as solvent refining, hydrorefining, and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil.

[0011] Group II base oils include, for example, paraffinic mineral oils obtained by a suitable combination of refining processes such as hydrorefining and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil.

[0012] Group III base oils and Group II+ base oils include paraffinic mineral oils manufactured by a high degree of hydrorefining in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil, base oils refined by the Isodewax process which dewaxes and substitutes the wax produced by the dewaxing process with isoparaffins, and base oils refined by the Mobil wax isomerisation process.

[0013] Examples of synthetic oils include polyolefins, polyoxyalkylene glycols such as polyethylene glycol or polypropylene glycol, esters such as di-2-ethylhexyl sebacate or di-2-ethylhexyl adipate, polyol esters such as trimethylolpropane esters or pentaerythritol esters, perfluoroalkyl ethers, silicone oils and polyphenyl ethers.

[0014] Polyolefins include polymers of various olefins or hydrides thereof. Any olefin may be used, and as examples mention may be made of ethylene, propylene, butene and α-olefins with five or more carbons. In the manufacture of polyolefins, olefins may be used singly or two or more kinds may be used in combination. Particularly suitable are the

polyolefins called poly-α-olefins (PAO). These are base oils of Group IV.

[0015] GTL (gas to liquid) base oils synthesised by the Fischer-Tropsch method of converting natural gas to liquid fuel have a very low sulphur content and aromatic content compared with mineral oil base oils refined from crude oil. Fischer-Tropsch derived base oils have a very high paraffin constituent ratio, and so have excellent oxidative stability.

[0016] As typical examples of animal and plant oils mention may be made of castor oil and rapeseed oil.

[0017] The various base oils may be used singly or in mixtures.

[0018] The grease comprises from 1 to 19wt% of a metal soap, wherein the weight percentage is based upon the weight of the grease. The present inventors have sought to reduce the amount of metal soap in the grease, so desirably the amount of metal soap is as low as possible whilst giving the desired grease properties. Suitably the grease comprises from 1 to 15wt% of a metal soap, more preferably from 1 to 10wt% of a metal soap, even more preferably from 1 to 5wt% of a metal soap and most preferably from 1 to 3wt% of a metal soap.

[0019] A metal soap is a metal salt of a fatty acid. More than one metal may be present in the soap such that the soap is a mixed metal soap. Suitable metals include lithium, sodium, potassium, magnesium, calcium, barium, zinc and aluminium. Preferred metals are lithium and calcium. The most preferred metal is lithium. Suitable fatty acids include C_{12}-C_{25} long chain fatty acids, which may be saturated or unsaturated, and which may contain substituents such as hydroxyl groups. Preferred fatty acids include lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxy stearic acid, oleic acid, linoleic acid and linolenic acid. Most preferred fatty acids are stearic acid and 12-hydroxy stearic acid. The fatty acids may be used as pure compounds or alternatively can be used as derived from fats such as tallow, coconut oil, palm kernel oil or olive oil.

[0020] The grease comprises from 1 to 19wt% of a dispersant, wherein the weight percentage is based upon the weight of the grease. The dispersant is used herein to thicken the grease. The dispersant is selected from a non-aqueous dispersant, a non-aqueous dispersant composite, and mixtures thereof. The present inventors have found that the combination of a metal soap and a non-aqueous dispersant and/or non-aqueous dispersant composite can provide an effective grease, whilst reducing the amount of metal soap that is required. The amount of dispersant is preferably greater than 2wt%, more preferably greater than 3wt%. The amount of dispersant is preferably less than 15wt%, more preferably less than 10wt%.

[0021] Non-aqueous dispersants (NADs) are typically polymers, also called stabilizing polymers, which are suitable for dispersing solids in a non-aqueous medium. Typically, conventional NADs are block type polymers. However, the compatibility of such conventional NADs with both the solids and the medium, is often insufficient, leading to a poor stability of the dispersion. Therefore, other types of NADs have been developed in which the to-be-dispersed particles are bound to the stabilizing polymer. Such stabilized particles are hereinafter referred to as non-aqueous dispersant composites (NADCs). Such NADCs are, for instance, disclosed in US 4,673,703. In US 4,673,703, it is stated that the stability of the NADC in hydrocarbon liquids is based on a steric mechanism. Similarly, GB 1,594,123 and GB 1,599,045 disclose coating compositions in which the film-forming material comprises polymer particles of colloidal dimensions which are stably dispersed by a steric mechanism in a non-aqueous liquid continuous phase in which the polymer particles remain dispersed as discrete entities. Since the performance of the products in the prior art in many non-aqueous media is insufficient, other types of NADs, particularly new types of NADCs, have been developed.

[0022] The NADs and NADCs suitable for use in the greases of the present invention have a better thickening effect in various apolar media compared with prior art NADs and NADCs.

[0023] The NADCs for use in the present invention consist of a core which is not soluble in apolar media and a covalently-bonded outer layer of a dispersing or stabilizing polymer that surrounds the core. Due to the good compatibility of the dispersing-polymer-part of the NADC with non-aqueous media, the stability of the resulting dispersion is guaranteed, whereby the compatibility of the dispersing polymer and the solid core was found to become less relevant due to covalent bonding. This allows for the production of the said NADCs that are fully compatible with non-aqueous media.

[0024] It has been found that specific NADs and NADCs, wherein the dispersing polymer-part contains both acidic and basic moieties show an exceptional thickening effect when dispersed in non-aqueous media. Accordingly, in one embodiment of the present invention, the NADCs used herein comprise a dispersing polymer that is covalently bonded to the core and wherein the dispersing polymer contains both acidic and basic moieties.

[0025] In another embodiment of the present invention, the dispersion polymer of the NADs and NADCs used herein contains one or more moieties derived from oil-soluble monomers, including monomers like bicyclic (meth)acrylate esters. Such NADs and NADCs have been found to be compatible with a variety of apolar media whereby the acid and base moieties were able to provide the desired thickening effect.

[0026] The NADs and NADCs used herein are useful as a thickener in various apolar, also called non-polar or non-aqueous media. Such apolar media is herein defined to have a dielectric coefficient of less than 7 at 20°C. Suitably it is a medium with a dielectric coefficient at 20°C of less than 6.5, 6, 5.5, 5, 4.5, 4, 3.5, or 3. The dielectric constant is measured in accordance with ASTM D150.

[0027] The NAD for use herein is a dispersing or stabilizing polymer. The NADCs consist of a core which is not soluble in said media, and said dispersing or stabilizing polymer that is covalently-bonded to said core. The dispersing polymer

is fully compatible with the apolar media to be thickened. It is noted that the term "not soluble" herein means that the core material in its pure form has a solubility in heptane of less than 5 g/l at 20 °C. In an embodiment the non-soluble core has a solubility in heptane of at most 2, 1, or 0.5 g/l at 20 °C. Fully compatible means that the dispersing polymer, when not bound to a core, has a solubility in heptane of at least 5 g/l at 20 °C. In an embodiment the dispersing polymer, when not bound to a core, has a solubility in heptane of 7, 10, or 15 g/l at 20 °C. In an embodiment, the solubility of the dispersing polymer increases with increasing temperatures.

[0028] In the NADCs, the dispersing polymer is located on the outside of the core, not necessarily in a shell-like structure, but the dispersing polymer will be located in a shell-like area surrounding the core. Especially when present in an apolar medium, they are believed to be able to form "fringes" or "tails" that stick into the medium, thus dispersing the core in said medium. Due to the good compatibility of the NAD and the dispersing-polymer-part of the NADC with non-aqueous media, the stability of the resulting dispersion is guaranteed, whereby the compatibility of the dispersing polymer and the solid core was found to become less relevant due to the covalent bonding. This allows the production of the NADCs described herein that are fully compatible with apolar media.

[0029] To achieve the desired thickening power of the NADs and NADCs in apolar media, the NAD or dispersing-polymer-part of the NADC must be derived from a mixture of monomers such that it contains both lyophilic, preferably oleophilic, monomers having an affinity for the apolar medium to be thickened, and one or more monomers with acidic and basic moieties. Accordingly, in one embodiment, the NADs are dispersing polymers and the NADCs comprise one or more dispersing polymers that are covalently bonded to the core and wherein the dispersing polymer contains lyophilic, preferably oleophilic, moieties, acidic, and basic moieties.

[0030] In an embodiment the NAD or dispersing polymer of the NADC is obtainable from a polymerization wherein a mixture of two or more monomers is present, as desired. The acid and basic groups can be introduced through two different types of monomer, each bearing either the acid or basic functionality or one monomer can bear both the acid and base functionality, as in betaines which have a polymerizable group or can be grafted onto a polymer. Alternatively, a prepolymer is made using one or more monomers with either acid or basic functionality, after which the resulting prepolymer is reacted with a reactant bearing groups capable of reacting with the prepolymer as well as groups of the other type of functionality, whereby part or all of the acid or base groups of the prepolymer are still present in the final polymer.

[0031] The ratio in which the acid and basic functions are present in the NAD or dispersing polymer can be varied within a wide range. Suitably the ratio of acid and basic groups ranges from 1:99 to 99:1 mole%. In an embodiment the molar ratio between acid and base groups of the polymer is more than 5:95, more than 10:90, more than 25:75, more than 40:60, or more than 50:50. In an embodiment the molar ratio between acid and base groups of the polymer is less than 95:5, less than 90:10, less than 80:20, less than 75:25, or less than 70:30. In an embodiment the acid and base groups are present in the polymer in a molar ratio between 50:50 and 70:30.

[0032] In an embodiment each dispersing polymer molecule comprises sufficient acid functions to generate the desired thickening effect. The number of acid functions on the polymer is suitably 1, 2, 3, 4, 5, 10, 20, 50 or more per polymer molecule. The number of acid functions on the polymer can be 1000, 100, 50, 20, 10, or less.

[0033] In an embodiment each dispersing polymer molecule comprises sufficient base functions to generate the desired thickening effect. The number of base functions on the polymer is suitably 1, 2, 3, 4, 5, 10, 20, 50 or more per polymer molecule. The number of base functions on the polymer can be 1000, 100, 50, 20, 10, or less.

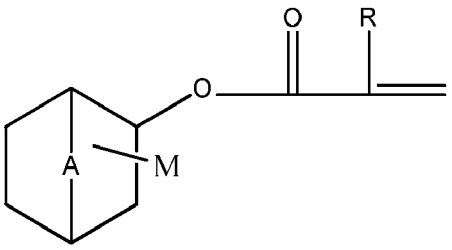
[0034] If the base function is an amine, then the number is suitably much higher than the amount of acid groups in the polymer. The number of base functions of the polymer can then be 30000, 10000, 5000, 2000, 1000, or less. Such polymers are characterized by a positive base number which is used in its conventional meaning and is a measure for the amount of free amine functions that can be reacted with acidic moieties. Suitably an excess of amine base function, compared to the acid function, is present in the dispersing polymer. Suitably the excess is such that when the amine function has reacted with the acidic function of the dispersing polymer, the excess results in a total base number of 6-90 mg/kg dispersing polymer. The base number is suitably determined in accordance with ASTM D 4739-02, optionally using a solution in heptane. When NADCs with a base number is used, the media in which it is used will have an anticorrosive effect and the media will remain a better viscosity when attached by acidic compounds.

[0035] In an embodiment the one or more acid functions of the polymer are obtained by polymerization of one or more monomers selected from unsaturated carboxylic acids, unsaturated sulfonic acids, unsaturated phosphoric acids, and unsaturated boric acids. Unsaturated carboxylic acids include acrylic acid, methacrylic acid, crotonic acid, tiglic acid, citronellic acid, ricin acid, oleic acid, palmitoleic acid, erucic acid, brassidic acid, vinylbenzoic acid, such as 4-vinylbenzoic acid, sorbic acid of formula $CH_3CH=CHCH=CHCOOH$, linolenic acid of formula $CH_3(CH_2CH=CH)_3(CH_2)_7CO_2H$, dihydrogeranic acid of formula $(CH_3)_2C=CHCH=CHC(CH_3)z=COOH$, maleic dicarboxylic acid, itaconic diacid, citraconic diacid, and mesaconic diacid, aconitic triacid $HOOC\text{-}CH_2C(COOH)=CHCOOH$, and any isomer of any of these compounds, salts thereof, and mixtures thereof. Unsaturated sulfonic acid monomers include 2-acrylamido-2-methylpropane sulfonic acid, vinyl sulfonic acid, 2-sulfoethyl acrylate, 2-sulfoethyl methacrylate, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, sodium styrene (4-)sulfonate, and 2-propene-1-sulfonic acid, and salts thereof, and combinations thereof.

Unsaturated phosphoric acids include phosphoric acid 2-hydroxyethyl (m)ethacrylate ester, and phosphoric acid esters of alkoxylated (m)ethacrylates.

[0036] In an embodiment the one or more base functions of the polymer are derived from monomers with primary, secondary, or tertiary amine groups. In an embodiment they are primary amine monomers selected from vinyl amine, lysine, allylamine, and 2-aminoethyl methacrylate. In an embodiment they are secondary amine monomers selected from N-methylvinylamine, tert-butylaminoethyl methacrylate (TBAEMA), and N-(3-aminopropyl)methacrylamide. In an embodiment they are tertiary amine monomers selected from dimethylaminopropyl methacrylamide (DMAPMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), dimethylaminopropyl methacrylate, 2-vinyl-1-methylpyridine, 2-dimethylaminoethyl(m)ethacrylate, and N-vinylpyrrolidone. Often the basic amine monomers are supplied in the salt form, usually with hydrochloric acid.

[0037] In an embodiment, at least one monomer selected from bicyclic (meth)acrylate esters being a (meth)acryloyl radical bonded to a six-membered carbon atom bridged ring is used when making the NAD or dispersing polymer. Such monomers are lyophilic and oleophilic. Said group of monomers include products like decahydronaphthyl (meth)acrylates, and adamantyl (meth)acrylates, but preferred are products according to formula (I)



wherein

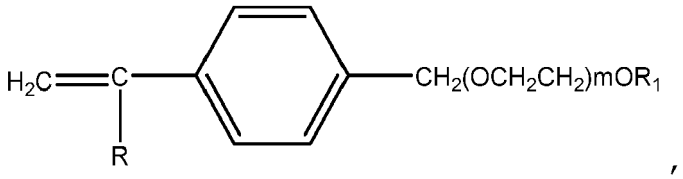
R is H or -CH_3,
A is -CH_2-, -$CH(CH_3)$- or -$C(CH_3)_2$-, and
one or more M is covalently bonded to any carbon of the bicyclic rings, preferably to a carbon atom of the six-membered ring, and each M is independently selected from the group consisting of hydrogen, halogen, methyl and methylamino group or a plurality thereof.

[0038] Non-limiting examples of the bicyclic (meth)acrylate esters include isobornyl (meth)acrylate, bornyl (meth)acrylate, fenchyl (meth)acrylate, isofenchyl (meth)acrylate, norbornyl methacrylate, cis, (endo) 3-methylamino-2-bornyl (meth)acrylate, 1,4,5,6,7,7-hexachlorobicyclo [2.2.1]-hept-5-ene-2-ol methacrylate (HCBOMA) and 1,4,5,6,7,7-hexachlorobicyclo [2.2.1]-hept-5-ene-2 methanol methacrylate (HCBMA), and mixtures of such bicyclic methacrylates. It is noted that the term (meth)acrylates as used herein is used to cover both the corresponding acrylate and methacrylate. The chlorinated compounds are less preferred since they can liberate corrosive HCl, depending on the circumstances. A preferred bicyclic methacrylate ester is isobornyl methacrylate. The bicyclic (meth)acrylate esters are known per se and may be prepared in known fashion or may be obtained from commercial sources. It was found that the use of these monomers when preparing the NAD or dispersing polymer of the invention results in a NAD and NADC having an enhanced thickening effect in a very wide range of apolar media.

[0039] In another embodiment one or more lyophilic monomers selected from oil-soluble monomers other than bicyclic (meth)acrylate esters is used. Suitable oil-soluble monomers include C_{10-18} alkyl (meth)acrylates or mixtures thereof, such as lauryl methacrylate, monomers having one or more 12-hydroxystearic acid residues, vinyl aromatic monomers such as styrene, tert-butyl styrene, tert-octyl styrene, and vinyltoluene, and hydrocarbon monomers such as isoprene and butadiene. Herein oil-soluble monomer means that the monomer will be miscible with heptane in a concentration of at least 25% by weight at 20 °C. Suitably they are miscible with heptane in a concentration of at least 75% by weight at 20°C. In an embodiment, the oil-soluble monomer is miscible with heptane in all concentrations at weight at 20°C.

[0040] Suitably the amount of bicyclic (meth)acrylate esters, or if not used the amount of oil-soluble monomers, or if both are used the total amount of bicyclic (meth)acrylate esters and oil-soluble monomers is 5 percent by weight (%w/w) or more of the total amount of monomers comprised in the dispersing polymer. In an embodiment, the total amount of bicyclic (meth)acrylate esters and oil-soluble monomers is 10, 20, 40, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 %w/w or more.

[0041] In an embodiment the NAD or dispersing polymer is produced by polymerizing a mixture of monomers that include vinyl silicones and vinyl benzyl ethers of the formula



wherein R is hydrogen or methyl, m=5-100, and R1 is an alkyl, alkaryl, or aralkyl group with 10-22 carbon atoms. The use of such monomers can allow a more constant thickening effect with varying temperatures in the application. In an embodiment these vinyl silicones and vinyl benzyl ethers make up from 0.01 to 25, 20, 15, 10, or 5 percent by weight (%w/w) of the total amount of monomers comprised in the dispersing polymer.

[0042] Other monomers than the ones mentioned above can be uses in any embodiment when making the dispersing polymer. These can be monomers that are (meth)acrylic, vinyl, or vinylidene based. In principle any other monomer containing the grouping CH2=C< can be used. These include C1-9 alkyl or hydroxyalkyl esters of (meth)acrylic acid, such as ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, butyl methacrylate, benzyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate, as well as acrylic acid and methacrylic acid themselves, other derivatives of those acids such as acrylonitrile, methacrylonitrile, acrylamide and methacrylamide, vinyl esters of organic and inorganic acids such as vinyl acetate, vinyl propionate, vinyl chloride and vinylidene chloride. Since the solubility of polymers based on C1-4-alkyl (meth)acrylates in oils is not good, in an embodiment the amount of such lower alkyl (meth) acrylates is kept low, suitably an amount of 0.01 to 25, 20, 15, 10, or 5 percent by weight (%w/w) of the total amount of monomers comprised in the dispersing polymer is used.

[0043] In another embodiment the use of higher alkyl (meth)acrylates in the dispersing polymer is preferred.

[0044] Albeit that the molecular weight of the dispersant polymer has an influence on how effectively it thickens, the dispersing polymer can have a molecular weight within a wide range. Typically the thickening power becomes higher as the molecular weight increases. Suitably the weight averaged molecular weight is at least 7000 D. In an embodiment the molecular weight is 10, 20, 50, 100. or 200 kD or more. The polydispersity of the polymer is typically in the range of 1.5-10. For polymers with a higher polydispersity the molecular weight is suitably towards the higher end of the range.

[0045] The average radius of gyration, or hydrodynamic volume, of the dispersing polymer (without attachment to a core), as determined by dynamic and static light scattering in oil, is suitably 20-200 nm. In an embodiment the radius of gyration of the polymer is 25-150 nm.

Core

[0046] The core can be any material not dissolving in the apolar medium and which allows the dispersing polymer to be chemically, preferably covalently, bonded thereto. The core is suitably a polymer. Any of the monomers mentioned for use in the dispersing polymer production, but not limited thereto, can be used when making a core polymer. In an embodiment the core polymer does not comprise acid and base monomers. In an embodiment the core is a cross-linked polymeric material. For guidance, it can be stated that crosslinking monomers used to make such a cross-linked polymer include allyl methacrylate, trimethylolpropane triacrylate (Sartomer® SR 351), diallyl phthalate, the aromatic diacrylate of bisphenol A (Photomer® 4028), ethylene glycol dimethacrylate and analogs thereof like hexanediol dimethacrylate, and divinylbenzene.

[0047] In an embodiment, the core polymer is not a polymer that is swellable and not soluble in the apolar medium. Swellable in apolar media is herein used for polymers which, when mixed with base oil 500n (Daesan) ex Shell (5g/50ml), and filtering of the mixture with a 150 ml, 60 mm diameter, glass-frit filter type P4 (with 10-16 micron pores) at 25°C, whereby the oil is removed by applying vacuum under the glass frit, followed by air being sucked through the polymer and the glass frit for 10 minutes, followed by a single rinse and stir with 50 ml ethanol and again pulling air through the polymer and the glass frit for 5 minutes, contain from 1 to 99 percent by weight (%w/w) of the base oil, based on the weight of the dry polymer. In an embodiment, the core polymer is not a swellable polymer which, after removal of the unbound oil as described above, contains more than 2, 3, 4 or 5 %w/w of the oil, based on the weight of the dry polymer. In an embodiment, the core polymer is not a swellable polymer which, after removal of the unbound oil, contains less than 75, 55, 40, 30, 25, 20, 15, or 10% w/w of the oil, based on the weight of the dry polymer. It is noted that the term "not soluble" of the core polymer means that the core material in its pure form, has a solubility in heptane of less than 5 g/l at 20°C.

[0048] In the process of preparing NADCs, the core can be pre-formed, meaning that first a core polymer is produced, which is subsequently reacted such that a dispersing polymer becomes attached to it. This reaction can be through any reactive group on the core polymer. The dispersion polymer may also be grafted onto the core. Suitably this grafting process is a conventional process in which in a first step a hydrogen atom is abstracted from the core polymer. In an embodiment the grafting process is achieved through a radical polymerization of monomers in the presence of the core

polymer. In another process hydrogen atoms are abstracted from both a core and a dispersion polymer. This is suitably done in an extruder.

[0049] Alternatively, the dispersing polymer is formed first after which parts of the dispersing polymer is reacted with further reactants to form a core polymer. This process can be a radical polymerization process using monomers as mentioned above, or it can be a condensation process, such as by condensing acid groups with polyols or reacting basic groups with polyacids, or an addition process, for instance reacting an isocyanate with part of the basic functions of the dispersing polymer. Such reactions of the dispersing polymer to form the NADC is suitably performed using an aqueous medium wherein the reactants are dispersed.

[0050] The average particle size of the core polymer, as measured in heptane using a Malvern multisizer, is 500 nm, 400, 300, 200, 100, or 50 nm or less. Suitably the particle size is 1, 2, 5, or 10 nm or more.

[0051] The weight ratio of core and dispersing polymer in the NADCs can be varied within a wide range. Suitably the ratio of core and dispersing polymer ranges from 1:99 to 99:1 %w/w. In an embodiment the weight ratio between core and dispersing polymer is more than 5:95, more than 10:90, more than 15:85, more than 20:80, or more than 25:75. In an embodiment the weight ratio between core and dispersing polymer is less than 90:10, less than 70:30, less than 50:50, less than 40:60, or less than 30:70. In an embodiment the core and dispersing polymer is present in a weight ratio between 10:90 and 30:70.

[0052] Any conventional polymerization process can be used to form the NADs and NADCs of the invention, see above for some particular elements. Suitably the polymerization of the NAD or NADC is conducted in the presence of a medium in which the dispersing polymer is fully compatible. Media that may be used include solvents containing 50 or more % by weight of one or more C7-C22 hydrocarbon, such as heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, and any of their isomers, such as tri isododecane. However, the medium suitably comprises other apolar solvents such as liquid propane, butane, pentane, hexane, but also toluene, xylene and oils may be used.

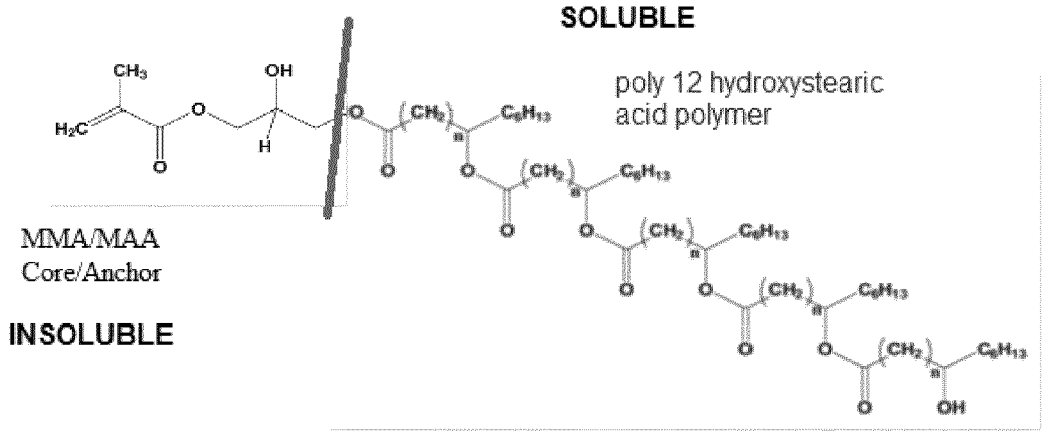
[0053] In view of potential environmental concerns, it is preferred not to use aromatic solvents in the medium. Also, in view of purification steps that may be needed to obtain the NAD and NADC, it can be beneficial not to use media which is difficult to separate from the NAD or NADC. Accordingly, in one embodiment the media is chosen so that it can be removed from the NAD or NADC by volatilization, i.e. evaporation, of the medium. This can be at lowered pressures and/or higher temperatures if desired. In an embodiment the media has a boiling point or boiling point range within the range of from -5 to 150 °C at 1 bara.

[0054] In another embodiment the lowest boiling point of the medium coincides with the polymerization temperature during the polymerization step. This allows the polymerization to be performed under reflux conditions, ensuring a good temperature control.

[0055] Suitably the medium, when removed from the product, is recycled to the polymerization step. Optionally is it purified before being used as a polymerization medium again. In an embodiment, the medium comprises heptane. However, depending on the dispersing polymer be made, it may be desired to use an aqueous process, such as an emulsion or suspension polymerization. It is noted that if making the dispersing polymer involves reactions with one or more isocyanates, it is preferred to use an organic medium and not an aqueous medium.

[0056] If an NADC is produced, the dispersing polymer is suitably made by polymerization of the monomers in the presence of the core polymer. In the polymerization, all monomers of the dispersing polymer can be added at once or they can be, wholly or partly, added consecutively, in any order and in any combination. Alternatively, the dispersing polymer is produced first, and then modified with an agent that will allow later reaction with monomers that make up the core. In any of these processes all the polymerization initiator, or constituents making up the initiating species, can be added at once or they can, wholly or partly, be added consecutively, in any order and in any combination. The initiating species can be conventional organic peroxides, redox-type initiators, and/or reagents allowing a living-type free radical polymerization. For ease of processing, conventional polymerization techniques are used, such as batch and semi-batch processes. Suitably all monomer is added at once and part of the initiating species, or one of its constituents, is added over time during the course of the polymerization.

[0057] Suitably an NADC used herein is formed by copolymerizing the lyophilic monomer of the formula



together with additional monomers to form a core that constitutes mainly of the other monomers which is stabilized by the hydroxystearic function, which is subsequently reacted with molecules providing acid and base functionality, e.g. by reaction with specific epoxides or isocyanates, or by radical reactions with monomers as presented above.

[0058] The grease may comprise one or more additives, in amounts normally used in this field of application, to impart certain desirable characteristics to the grease including oxidation stability, tackiness, extreme pressure properties, corrosion inhibition, reduced friction and wear, and combinations thereof. The grease suitably comprises from 0.1wt% to 15wt%, preferably from 0.1wt% to 5wt%, more preferably from 0.1wt% to 2wt%, and even more preferably from 0.2wt% to 1wt% of one or more additives, based upon the weight of the grease.

[0059] Suitable additives include one or more extreme pressure/antiwear agents, for example zinc salts such as zinc dialkyl or diaryl dithiophosphates, borates, substituted thiadiazoles, polymeric nitrogen/phosphorus compounds made, for example, by reacting a dialkoxy amine with a substituted organic phosphate, amine phosphates, sulphurised sperm oils of natural or synthetic origin, sulphurised lard, sulphurised esters, sulphurised fatty acid esters, and similar sulphurised materials, organo-phosphates for example according to the formula $(OR)_3P=O$ where R is an alkyl, aryl or aralkyl group, and triphenyl phosphorothionate; one or more overbased metal-containing detergents, such as calcium or magnesium alkyl salicylates or alkylarylsulphonates; one or more ashless dispersant additives, such as reaction products of polyisobutenyl succinic anhydride and an amine or ester; one or more antioxidants, such as hindered phenols or amines, for example phenyl alpha naphthylamine, diphenylamine or alkylated diphenylamine; one or more antirust additives such as oxygenated hydrocarbons which have optionally been neutralised with calcium, calcium salts of alkylated benzene sulphonates and alkylated benzene petroleum sulphonates, and succinic acid derivatives, or friction-modifying additives; one or more viscosity-index improving agents; one or more pour point depressing additives; and one or more tackiness agents. Solid materials such as graphite, finely divided MoS_2, talc, metal powders, and various polymers such as polyethylene wax may also be added to impart special properties.

[0060] The grease may be produced using commonly known grease production methods. In a first method, a metal soap, the non-aqueous dispersant/non-aqueous dispersant composite and any additives are mixed with the base oil to form the grease. In a second method, the metal soap is formed in situ. A metal salt and the fatty acid are added the base oil and saponification occurs to generate the metal soap in the base oil. The non-aqueous dispersant/non-aqueous dispersant composite and any additives may be added before, during or after production of the metal salt in the base oil. Heating may be used to ensure all components are melted and thereafter to dehydrate the composition. Blending is effected through vigorous stirring and the mixture allowed to return to room temperature. Homogenisation of the resulting grease composition may be required and, if so, is typically performed using a roll mixer, such as a three-roll mill or a high pressure homogeniser. The grease may be subjected to further finishing procedures such as filtration and deaeration.

[0061] The penetration of the grease (unworked and worked) may be measured using ASTM D 217. Preferably the worked penetration of the grease at 25°c (60 strokes) is from 200 to 400 tenths of a mm, more preferably from 220 to 340 tenths of a mm. Such penetrations are typical of grease compositions having grades 1 to 3 in the NLGI classification.

[0062] The dropping point of the grease may be measured using ASTM D 2265 or IP 396. The dropping point is preferably as high as possible, e.g. from 160 to 200°C or higher.

[0063] The grease of the invention is suitably used in typical applications for lubricating greases such as in constant-velocity joints, ball joints, wheel bearings, alternators, cooling fans, ball screws, linear guides of machine tools, sliding areas of construction equipment, and bearings and gears in steel equipment and various other industrial mechanical facilities.

[0064] It is noted that any one of the embodiments mentioned herein can be combined with any other embodiment mentioned herein. When a ratio or amount in given it is by weight, unless specified otherwise.

[0065] The invention is further explained in detail below by means of examples, but the invention is in no way limited by these examples.

Examples

[0066] A representative NAD preparation is given below. It is related to the methods given in the book "Dispersion polymerization in organic media" (edited by K.E.J. Barrett, John Wiley & Sons, 1975), pages 106-114 for the dispersant polymer and functionalization, and pages 234-241 for the formation of the NAD. The following acronyms are used:

LMA	lauryl methacrylate (oil-soluble monomer)
SMA	stearyl methacrylate
iBXMA	isobornyl methacrylate
MAA	methacrylic acid
BA	butyl acrylate
DMAPMA	dimethylaminopropyl methacrylamide
DMAEMA	dimethylaminopropyl methacrylate
HPMA	hydroxypropyl methacrylate
DiMeAm	dimethylacrylamide
HDDMA	1,6-hexanediol dimethacrylate
AA	acrylic acid
BMA	butyl methacrylate
MMA	methyl methacrylate
St	styrene

[0067] MVIN 170 and Hygold L750 are group V oils. Hygold L750 is a naphthenic base oil with an aniline point of about 99°C. MVIN 170 has an aniline point of about 99.9°C.

Preparation of Dispersing Polymer (NAD)

[0068] A 3-1, 4-neck round bottom flask is equipped with a stainless steel stirrer, thermometer, a condenser, a heating media, a slow add funnel and a syringe pump. After assembly, 158 g of heptane is added followed by 350 g of a mixture of monomer as mentioned in the table below. The addition vessels are rinsed/flushed with 11 g of heptane. The mixture is brought to reflux and after 5 minutes 60% of a mixture of 2.3g of Trigonox® 125 - C25 (t-amyl peroxypivalate) and 210 g of heptane is added over a period of 15 minutes. The mixture is held at reflux for 1 h then the remaining 40% of the initiator is added over 4 h. Then 447 g of heptane is added and 5 minutes after reflux started again, a mixture of 0.5 g of Trigonox® 125 - C25 and 20g of heptane was added over 4 hours followed by a one hour reaction time.

Functionalization of NAD

[0069] To 1030 g of the stabilizer polymer solution are added 1.5 g of Arquad® HC (di(hydrogenated tallow)dimethylammonium chloride), glycidyl methacrylate in an amount as specified, (for example 2 the amount would be 0.42g, and 15 g of heptane. The addition devices are rinsed/flushed with 0.18 g of 2-(t-butyl)-4,6-dimethyl phenol in 15 g of heptane. The mixture is held at reflux for 8 hours after which up to 440 g of heptane is added, dependent on the desired viscosity.

Preparation of NADC

[0070] To 1490 g of the functionalized NAD solution, a mixture of 94 g of heptane, 10% of a solution of a core mixture comprising 45g of a core monomer mixture of methyl methacrylate and/or (co)monomer as indicated (in example 2 a mixture of MMA and AA in a weight ratio of 75/25), and the indicated amount of hexanediol dimethacryate crosslinking agent) (for example 2 the amount would be 0.63g) is added over 20 minutes. The mixture is held at reflux. At the start of dosing this core mixture, also the dosing starts of an initiator mixture of 1.44 g of Trigonox® 125 - C25 in 102 g of heptane. The initiator mixture was added over a 5 hour period. After 40 minutes of the start of the addition of the initiator, the remaining 90% of the core mixture is added over a 3 h period.

Oil Exchange

[0071] The NADCs of the above procedures are exchanged into oil solutions using a rotatory evaporator. The desired oil is added to the solution in heptane in a calculated amount so the final active level of the NADC in the oil is 15.0%w/w

after distilling off the heptane.

[0072] In some systems, the substitution of heptane with the oil results in the formation of a precipitate of the NAD polymer, and in other cases the formation of a semi-translucent precipitate, corresponding to a swollen polymer, which often coexists with free oil. For these systems, the compatibility was noted as poor and such systems were not tested for solution viscosities.

Viscosity Measurements

[0073] The measurements are conducted with a Brookfield RV viscometer with a Heliopath accessory at room temperature using a spindle type C, on clear, i.e. compatible, 15% solutions or dispersions of dispersing polymers and NADCs in oil. If the viscosity is too high to be accurately measured with a spindle C, then a spindle D can be used.

Table 1

	Monomers used to make the dispersing polymer (mole%)							Functionalization agent	Core polymer			Brookfield viscosity (Pas)			
Example #	iBXMA	SMA	LMA	Acid monomer MAA	BA	basic monomer (DMAP-MA)	Other monomer	GMA (mole % on dispersing polymer	HDDMA XI agent, mol % on core monomers	comonomer	comonomer, wt %	MVIN 170		Hygold L750	
CE A	0	34,15	40,7	7,7	7,5	0	HPMA 5 DMeAm 5	0,840	0,2	AA	25	good	44	good	4
CE B	0	37, 9	45,3	8	7,8	0	St 1	0,330	0,2	AA	25	good	109	n.d.	n.d.
CE C	47	10,7	17,2	7, 7	7,5	0	HPMA 5 DMeAm 5	0,053	0,5	BMA	25	o	n.d.	o	n.d.
CE D	47	10,7	17,2	7,7	7,5	0	HPMA 5 DMeAm 5	0, 139	1,5	BMA	25	good	1	o	n.d.
Ex1	27	10,2	16, 8	7,7	7,5	3,8	St 27	0,157	0,25	BMA	25	n.d.	n.d.	good	9
Ex2	47	13,7	20,3	7,7	7,5	3,8		0,190	0,5	AA	25	good	844	good	1390
Ex3	47	13,7	20,3	7,7	7,5	3,8		0,192	0,5	BMA	25	good	288	good	185
Ex 4	47	12,7	19,3	7,7	7,5	3.9 DMAEMA		0,150	0,5	AA	25	n.d.	n.d.	good	23
Ex 5	58,3	8,1	14,7	7,7	7,5	3,8		0,070	0,5	AA	25	good	359	n.d.	n.d.
Ex 6	58,3	8,1	14,7	7, 7	7, 5	3,8		0,049	0	BMA	25	good	462	n.d.	n.d.
n.d. = not determined; o=not as good															

[0074] While the NADCs show compatibility and low viscosity in heptane, the medium of preparation, their behaviour in different oils varies greatly (Table 1).

[0075] NADCs based on long chain alkyl methacrylates, LMA and SMA combined with an acidic monomer, even when used with a monomer with hydroxyl or amide functions (Comparative Examples A-D) showed reasonable to good compatibilities in the types of oils that were tested, but exhibited too little viscosifying or thickening power. With 27 mol % iBXMA, along with 27 mol % St, and including a basic monomer of the invention, the polymer of Example 1 showed better properties.

[0076] Example 3, when compared to Example 1, shows that increasing the amount of iBXMA improved the thickening effect of the NADC. This was confirmed in Example 6. Also in Examples 2-4 the improved properties were observed, but it was realized that the basic monomer that is used influences performance to a certain extent. Example 5 shows that the amount of crosslinker in the core of the NADC can have an influence on the dispersibility of the NADC, but Example 6 shows this can be compensated by adapting the dispersing polymer part. Hence some routine optimization may be needed for a specific core material, by varying the monomer levels of the dispersing polymer.

[0077] Thus, it is found that the incorporation of a relatively small amount of both acidic and basic monomers in combination with one or more lyophilic monomers and optional further monomers in the dispersing polymer (or the dispersing polymer part of an NADC) allows for obtaining a great thickening efficacy of apolar media.

Grease Examples

[0078] A variety of grease examples were prepared as set out in Table 2 below using certain of the dispersant molecules from Table 1 above.

[0079] In Table 2 below the following abbreviations are used:

NAD Reference: The example number of the dispersant molecule which is used in Table 1 above
LiHSA = Lithium hydroxystearate
NAD = non-aqueous dispersant
Base Oil HAS = base oil in which the Lithium hydroxystearate is provided in
Base Oil NAD = base oil in which the non-aqueous dispersant is provided in
Mixed = mixture of HVI650, HVI160s, MVIN170, Daesan 500N in varying amounts
HVI650 = base oil commercially available from Shell
HVI160s = base oil commercially available from Shell
MVIN170 = base oil commercially available from Shell
Daesan 500N = base oil commercially available from Shell Chemicals
Chevron 600R = base oil commercially available from Chevron
MotivaStar 12 = base oil commercially available from Motiva
Hygold L750 = base oil commercially available from Ergon
Penetration uw = Unworked Penetration measured in accordance with ASTM D217
Penetration w = Worked Penetration measured in accordance with ASTM D217
Delta = Difference between Unworked Penetration and Worked Penetration
Dropping Point = Measured in accordance with IP396.

Table 2

Example	NAD reference	LiHSA %w	NAD %w	Base oil HSA	Base oil NAD	Penetration uw/w / dmm	Delta	Dropping Point / °C
Comparative Example 1	----	5	---	MotivaStar 12	---	>475/>475	----	146
Comparative Example 2	----	10	---	MotivaStar 12	---	332/316	-16	200
Comparative Example 3	---	10	---	DAESAN 500N	---	305/294	-11	201
Comparative Example 4	---	10	---	DAESAN 500N	---	320/319	-1	201
Comparative Example 5	---	5	---	DAESAN 500N	---	>475/>475	--	--

(continued)

Example	NAD reference	LiHSA %w	NAD %w	Base oil HSA	Base oil NAD	Penetration uw/w / dmm	Delta	Dropping Point / °C
Grease Example 1	Ex. 1	5	5	Mixed	Hygold L750	313/327	14	190

Discussion

[0080] Comparative Examples 1 to 5 illustrate the effect of LiHSA and its ability to form lubricating grease from the selected base oils. Addition of 10%w of LiHSA to base oil gives well-structured grease samples with high dropping points and excellent mechanical stability. Upon addition of only 5%w of LiHSA no suitable grease is obtained (penetration >475dmm, Comparative Example 1 and 5).

[0081] Upon addition of 5%w NAD to a grease containing 5%w LiHSA, a well-structured grease is obtained, which exhibits a good mechanical stability and a high dropping point (Grease Example 1). Hence this invention enables an excellent grease to be produced using lower levels of LiHSA.

Claims

1. A grease comprising:

(a) greater than 60wt% of a base oil;
(b) from 1 to 19wt% of a metal soap; and
(c) from 1 to 19wt% of a dispersing polymer,

wherein the weight percentages are based upon the weight of the grease.

2. A grease according to Claim 1 wherein the dispersing polymer comprises lyophilic, base and acid groups.

3. A grease according to Claim 2 wherein one or more of the lyophilic groups are oleophobic groups.

4. A grease according to Claim 2 or 3 wherein the one or more acid groups are derived from one or more monomers selected from unsaturated carboxylic acids, unsaturated sulfonic acids, unsaturated phosphoric acids, and unsaturated boric acids.

5. A grease according to any of Claims 2 to 4 wherein the one or more base functions of the polymer are obtained from one or more monomers with basic hydroxyl or amine functions, preferably selected from the group consisting of monomers with primary, secondary, or tertiary amine groups.

6. A grease according to any of Claims 2 to 5 wherein the one or more lyophilic functions of the polymer are obtained from one or more monomers selected from the group consisting of bicyclic (meth)acrylate esters, linear or branched, substituted or unsubstituted, C10-22-alkyl (meth)acrylates, including monomers having one or more 12-hydroxystearic acid residues, vinyl aromatic monomers and hydrocarbon monomers.

7. A grease according to any of Claims 2 to 6 wherein the ratio of acid and basic groups ranges from 0.1:99.9 to 99:1 mole%.

8. A grease according to any of Claims 2 to 7 wherein the amount of acid and basic groups per polymer molecule, independently, ranges from 1 to 1000.

9. A grease according to any of Claims 2 to 8 wherein the dispersing polymer has a weight averaged molecular weight of at least 7000 D.

10. A grease according to any of Claims 6 to 9 wherein the amount of bicyclic (meth)acrylate esters, linear or branched, substituted or unsubstituted, C10-22-alkyl (meth)acrylates, including monomers having one or more 12-hydroxystearic acid residues, vinyl aromatic monomers and hydrocarbon monomers in the monomer mixture to make the

polymer is 5% by weight or more.

11. A grease according to any of Claims 2 to 10 wherein part or all of the lyophilic groups are derived from bicyclic (meth)acrylate esters.

12. A grease according to any of Claims 1 to 11 wherein the dispersing polymer is covalently bonded to a core polymer, whereby the weight ratio of the dispersing polymer to core polymer is from 1:99 to 99:1.

13. A grease according to any of Claims 1 to 12, wherein the metal in the metal soap is lithium or calcium.

14. A grease according to any of Claims 1 to 13 wherein the metal in the metal soap is lithium.

15. A grease according to any of Claims 1 to 14, wherein the metal soap includes a fatty acid chosen from one or more of lauric acid, myristic, palmitic acid, stearic acid, 12-hydroxy stearic acid, oleic acid, linoleic acid and linolenic acid.

16. A grease according to Claim 15 wherein the fatty acid is 12-hydroxy stearic acid.

17. A grease according to any of Claims 1 to 16, comprising from 1 to 5wt% of the metal soap.

18. A grease according to any of Claims 1 to 17, comprising from 3 to 10wt% of the dispersing polymer.

19. Use of a grease according to any of Claims 1 to 18 for lubricating a bearing.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 17 18 0781

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 Y	WO 2005/090531 A1 (LUBRIZOL CORP [US]) 29 September 2005 (2005-09-29) * page 9, line 8 - line 14; claim 1 * * page 5, line 5 - line 8 * * page 10, line 26 - line 30 * * page 12, line 3 - line 7 * * page 3, line 8 - line 9 * * claim 1; examples 1-5 *	1-11, 13-19 12	INV. C10M123/04
X Y	EP 2 695 932 A1 (NANOL TECHNOLOGIES OY AB [FI]) 12 February 2014 (2014-02-12) * paragraph [0045] - paragraph [0056]; table 2 *	1-11, 13-19 12	
Y	US 2010/167970 A1 (STOEHR TORSTEN [DE] ET AL) 1 July 2010 (2010-07-01) * claims 1, 17-19 *	12	

TECHNICAL FIELDS SEARCHED (IPC)

C10M
C10N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 November 2017	Klaes, Daphne

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 17 18 0781

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.

20-11-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005090531 A1	29-09-2005	EP 1725638 A1	29-11-2006
		JP 5121052 B2	16-01-2013
		JP 2007529603 A	25-10-2007
		JP 2011236441 A	24-11-2011
		US 2005209114 A1	22-09-2005
		WO 2005090531 A1	29-09-2005
EP 2695932 A1	12-02-2014	EP 2695932 A1	12-02-2014
		EP 2882833 A1	17-06-2015
		WO 2014023707 A1	13-02-2014
US 2010167970 A1	01-07-2010	BR PI0615243 A2	10-05-2011
		CA 2617554 A1	08-03-2007
		CN 101189268 A	28-05-2008
		DE 102005041528 A1	01-03-2007
		EP 1919961 A1	14-05-2008
		JP 5452921 B2	26-03-2014
		JP 2009506179 A	12-02-2009
		KR 20080049723 A	04-06-2008
		US 2010167970 A1	01-07-2010
		WO 2007025837 A1	08-03-2007

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 4673703 A **[0021]**
- GB 1594123 A **[0021]**
- GB 1599045 A **[0021]**

Non-patent literature cited in the description

- Dispersion polymerization in organic media. John Wiley & Sons, 1975, 106-114 **[0066]**