

(19)



(11)

EP 3 293 246 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

14.03.2018 Bulletin 2018/11

(51) Int Cl.:

C10M 115/08 (2006.01)

(21) Application number: **16188542.1**

(22) Date of filing: **13.09.2016**

(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: **BASF SE**

67056 Ludwigshafen am Rhein (DE)

- **BOYKO, Volodymyr**
68159 Mannheim (DE)
- **LUETH, Sabine**
67227 Frankenthal (DE)
- **WESTERHAUS, Felix Alexander**
67063 Ludwigshafen (DE)
- **RUEHLE, Thomas**
68259 Mannheim (DE)
- **REINHOLD, Frank**
48187 Canton (US)
- **ERNST, Martin**
69121 Heidelberg (DE)

(72) Inventors:

- **HANSCH, Markus**
67346 Speyer (DE)
- **RANFT, Meik**
68723 Schwetzingen (DE)

(74) Representative: **BASF IP Association**
BASF SE
G-FLP-C006
67056 Ludwigshafen (DE)

(54) LUBRICANT COMPOSITIONS CONTAINING DIUREA COMPOUNDS

(57) The presently claimed invention relates to the use of diurea compounds with a high degree of branching as thickening agents for lubricant compositions and grease compositions as well as lubricant compositions and grease compositions containing the diurea compounds.

Description

[0001] The presently claimed invention relates to the use of diurea compounds with a high degree of branching as thickening agents for lubricant compositions and grease compositions and as well as lubricant compositions and grease compositions containing the diurea compounds.

[0002] Lubricants are usually classified into four types: solid, semi-solid, gaseous and liquid lubricants. Liquid lubricants such as oil based lubricants and the semi-solid lubricants such as greases find wide application and are the most commonly used classes of lubricants.

[0003] An oil based lubricant is the best and preferred choice for the lubrication of gearing and is universally recognized as the most reliable lubricant by gearing and bearing experts. The concept of lubrication is based on providing a friction-reducing film, and liquid lubricants in the form of an oil provide the optimum distribution of a film.

[0004] Greases are used for lubricating and protecting mechanical machinery as an alternative to liquid lubricants, particularly when a lack of space or problems connected with dripping makes it difficult to use oil. A grease is defined as a solid to semi-fluid product of a dispersion of a thickening agent in a liquid lubricant, where other ingredients imparting special properties may be present. Thus, grease is not clear. Moreover, greases exhibit shear-thinning rheological properties, which means that the apparent viscosity of the grease reduces under shear.

[0005] Lubricants are often subjected to mechanical shearing, for example in automotive engines. This shearing causes lubricants to lose their viscosity. When subjected to sufficiently large number of cycles of shear, the viscosity may drop below acceptable levels and may call for replacement, failing which, surfaces may become prone to higher wear. Even lubricants that have consistent viscosity through a wide temperature range (high viscosity index) may still be susceptible to loss of viscosity when subjected to mechanical shearing. Oils that show a lower drop in viscosity over the duration of test are said to have better shear stability than oils that exhibit a relatively higher drop in viscosity.

[0006] Viscosity modifiers such as polymers are added to oil based lubricants to enhance viscosity index of the lubricating oil, but these polymers are not shear stable. Urea compounds find application as thickeners and viscosity modifiers in grease compositions but they have not been reported as thickeners for oil based lubricants. These compounds include the urea group (-NHCONH-) in their molecular structure. Grease compositions contain mono-, di- or polyurea compounds, depending upon the number of urea linkages.

[0007] EP 2 467 461 teaches lubricating grease composition for dual mass flywheel application comprising a mixture of a) at least 30% of base oil; b) 2 to 20% by weight of urea compound having density in the range of 850 to 1050 Kg/m³, based on total weight of the lubricating composition, wherein the difference in the densities of base oil and diurea compound is less than 50 Kg/m³. The diurea compound is prepared by reacting diisocyanate with a mixture of monoamines comprising C₆-C₁₀ and C₁₄-C₂₀ aliphatic monoamine, the preferred ones being C₈ aliphatic amine and C₁₈ aliphatic amine.

[0008] EP 1 602 710 relates to a lubricating grease for power steering apparatus. A grease composition is described that includes a) at least 70 % of base oil, b) 3 to 40 weight % of a diurea thickener c) at least 3 weight % of non-polar wax and d) at least 2 weight % of a polar wax. For the diurea compound, the preferred alkyl group is *n*-octyl or a straight chain C₁₂-C₂₀ in 1: 4 to 4: 1 mole ratio.

[0009] EP 2 716 745 discloses a grease composition applicable for fluorine compound refrigerant atmosphere comprising a base oil and diurea compound as a thickener. The content of the diurea thickener is in the range from 5 to 25% based on total amount of grease. It is further stated that in order to restrain elution, it is preferred that at least 10 % by weight of the alkyl groups present in the diurea compound is occupied by a monovalent alicyclic hydrocarbon group having 6 to 12 carbon atoms.

[0010] US 2014/0254968 teaches a grease composition containing diurea compound which is a mixture of an aliphatic diurea compound and an alicyclic diurea compound. The ratio of the aliphatic diurea compound to the alicyclic diurea compound considerably affects the bearing temperature, and in case where the proportion of the alicyclic diurea compound exceeds 50% by mole, the bearing temperature rises considerably. Meanwhile, the lower the proportion of the alicyclic diurea compound, the more the grease softens upon shearing. In case where the proportion thereof is less than 30%, the grease has especially high shear flowability and is less apt to form an oil film.

[0011] US 8,044,005 teaches a grease composition, for a rolling bearing, containing a base oil and diurea compound as thickening agent. The diurea compound is employed in an amount of 5 to 20 % by weight, based on total weight of the lubricant composition. It is mentioned that if the amount of diurea compound is less than 5 weight %, the lubricant composition is liable to soften and if the amount is more than 20 weight %, the lubricant composition becomes hard.

[0012] US 7,786,058 discloses a grease composition comprising a thickener which is a mixture of a) diurea compound having an average molecular weight between 500-750 g/mol in which 10-70% by mole of the linear hydrocarbon groups are unsaturated components, b) fatty acid metal salt, and c) aliphatic amide and bisamides. It further states that if the average molecular weight of the diurea thickener is less than 500 g/mol or exceeds 750 g/mol, optimal grease intervention and stable torque characteristics are not obtained.

[0013] US 5,059,336 relates to a grease composition for high speed anti-friction bearing containing in a base oil, A) 2 to 30 weight % of thickening agent consisting of a diurea compound, B) 0.2 to 30 weight % of sorbitan monooleate,

C) 0.2 to 3 weight % of barium sulfonate, and D) 0.2 to 3 weight % of barium lanolate, each weight % based on the total weight of the composition. It further discloses that if the content of the diurea compound is less than 2 weight %, its effects as thickening agent is nil whereas if it exceeds 30 weight %, the composition becomes too hard to be used as grease.

5 [0014] US 4,668,411 discloses a grease composition comprising a lubricating oil and a diurea thickener. The diurea compound is prepared by reacting a diisocyanate compound with cyclohexylamine and monoalkylphenylamine wherein the alkyl portion has 8 to 16 carbon atoms. It states that the characteristics of the grease prepared with use of the diurea compound differ greatly depending upon the chemical structure of the alkyl groups. When the alkyl groups have at least 12 carbon atoms each, the grease markedly softens and is therefore unusable at high temperatures and when each 10 alkyl group has up to 11 carbon atoms, the grease is fibrous, liable to scatter under high-speed conditions and therefore has a shortened life.

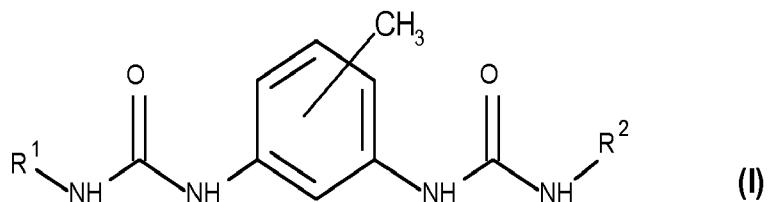
[0015] A measure of a lubricant's protective value is its ability to withstand shearing under pressure. Shear stability describes a lubricant's ability to resist a decrease in viscosity due to exposure to mechanical loads.

15 [0016] Due to ever increasing demands for higher performance, it would be desirable to provide novel highly effective thickening agents that are compatible with a wide range of base oils and, hence, when used in a lubricant composition, allow for the preparation of a lubricant composition showing a desired viscosity along with high shear stability.

[0017] Accordingly, it was an object of the presently claimed invention to provide novel highly effective thickening agents that are compatible with a wide range of base oils and, hence, when used in a lubricant composition, allow for the preparation of a lubricant composition showing a desired viscosity along with high shear stability.

20 [0018] Surprisingly it was found that diurea compounds having a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11 are compatible with a wide range of base oils, in particular base oils from Group III, IV and V; show improved thickening properties, i.e. even when added in small quantities to a lubricant composition the viscosity is increased; and lead to lubricant compositions that are shear stable. The novel diurea compounds of the present invention impart viscoelasticity to the lubricant compositions.

25 [0019] Thus, in one embodiment the presently claimed invention is directed to the use of at least a compound of general formula (I) as thickening agent



wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁₄-C₄₀-alkyl, or

40 R¹ is linear or branched, substituted or unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyiso-butene, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11 .

45 [0020] When the diurea compound of general formula (I) having a mean degree of branching in the range of ≥ 3 to ≤ 9 is used as a thickener, it imparts the desired thickening effect. By 'desired thickening effect' it is meant that the viscosity of the lubricant composition can be controlled by the amount of the diurea compound added to the base oil. For oil based lubricants, a quantity in the range of ≥ 0.2 to ≤ 1.5 % by weight imparts the viscosity required for the applications intended for oil based lubricants. For grease based lubricants, the thickening effect desired to impart consistency to grease formulation is achieved by adding higher quantity, in the range of ≥ 2 to ≤ 20 % by weight.

50 [0021] By the term "lubricant composition", in the sense of the presently claimed invention, is meant a composition which is capable of reducing friction between surfaces.

[0022] By the term "thickening agent", it is meant a compound which when added, increases the viscosity of the composition, in particular the viscosity of a lubricant composition and the viscosity of greases.

55 [0023] The term "viscoelastic" refers to those viscous fluids having elastic properties, i.e., the liquid at least partially returns to its original form when an applied stress is released.

[0024] The kinematic viscosity of the inventively claimed lubricant composition at 100 °C is preferably in the range of ≥ 1 to ≤ 100 mm²/s, more preferably in the range of ≥ 1 to ≤ 40 mm²/s, as determined in accordance with ASTM D445.

[0025] The unworked penetration of grease composition at 25 °C is in the range of 85-450 in accordance with ISO

2137:1985-11.

[0026] Unworked penetration is measured when a sample of grease is brought to 25 °C and transferred to a standard cup; its surface is smoothed and the cone, in its penetrometer assembly, placed so that its tip just touches the level grease surface. The cone and its movable assembly are permitted to rest on top of the grease for exactly five seconds.

5 The distance dropped is measured and recorded as the unworked penetration level.

[0027] The term "visibly viscous" refers to increase in viscosity observed visually, for a solution prepared by adding to the base oil the compounds of general formula (I) in comparison to the base oil alone.

[0028] Preferably at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 10 , more preferably in the range of ≥ 3 to ≤ 9 .

10 [0029] The mean degree of branching (iso-index) of the compounds of general formula (I) is essential to the invention since a mean degree of branching which is not too low is important in the compounds of general formula (I) according to the present invention to effect both solubility and sufficient shear stability in base oils.

[0030] In the context of the present invention, the mean degree of branching is generally defined as the number of methyl groups in a molecule of the alcohol minus 1. The mean degree of branching is the statistical mean of the degrees 15 of branching of the molecules of a sample.

[0031] The mean degree of branching can be determined by $^1\text{H-NMR}$ spectroscopy as follows: A sample of the alcohol or alcohol mixture, for instance the C_{17} alcohol or the C_{17} alcohol mixture, is first subjected to a derivatization with trichloroacetyl isocyanate (TAI). This converts the C_{17} alcohols to the carbamic esters.

20 [0032] The signals of the primary alcohols esterified in this way are at $\delta=4.7$ to 4.0 ppm, those of esterified secondary alcohols (where present) at about 5 ppm, and water present in the sample reacts with TAI to give the carbamic acid. All methyl, methylene and methine protons are in the range from 2.4 to 0.4 ppm. The signals <1 ppm are assigned to the methyl groups. From the spectrum thus obtained, it is possible to calculate the mean degree of branching (iso index) as follows:

25
$$\text{iso index} = ((F(\text{CH}_3)/3)/(F(\text{CH}_2\text{OH})/2)) - 1$$

where $F(\text{CH}_3)$ is the signal area corresponding to the methyl protons and $F(\text{CH}_2\text{OH})$ is the signal area of the methylene protons in the CH_2OH group.

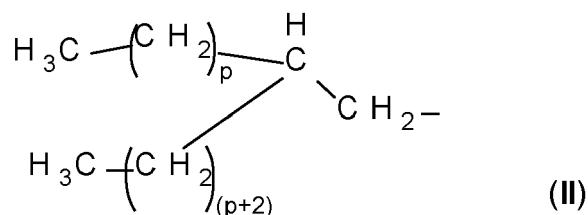
[0033] Preferably, R^1 and R^2 , independently of one another, are branched, substituted or unsubstituted $\text{C}_{14}\text{-C}_{40}$ alkyl or R^1 is branched, substituted or unsubstituted $\text{C}_{8}\text{-C}_{40}$ alkyl and R^2 is $\text{C}_{35}\text{-C}_{200}$ polyisobutene.

[0034] As used herein, "branched" denotes a chain of atoms with one or more side chains attached to it. Branching occurs by the replacement of a substituent, e.g., a hydrogen atom, with a covalently bonded aliphatic moiety.

[0035] In connection with "alkyl", the term "substituted" within the scope of this invention is understood as meaning the substitution of hydrogen by 1, 2, 3, 4 or 5 substituents selected from the group consisting of F, Cl, Br, I, CN, NH_2 , $\text{NH-C}_{1-6}\text{-alkyl}$, $\text{NH-C}_{1-6}\text{-alkylene-OH}$, $\text{N}(\text{C}_{1-6}\text{-alkyl})_2$, $\text{N}(\text{C}_{1-6}\text{-alkylene-OH})_2$, NO_2 , SH , $\text{S-C}_{1-6}\text{-alkyl}$, S-benzyl , $\text{O-C}_{1-6}\text{-alkyl}$, $\text{O-C}_{1-6}\text{-alkylene-OH}$, $=\text{O}$, O-benzyl , $\text{C}=\text{O}\text{C}_{1-6}\text{-alkyl}$, CO_2H , $\text{CO}_2\text{-C}_{1-6}\text{-alkyl}$, phenyl or benzyl. The substitution of hydrogen occurs either on different atoms or on the same atom, for example trisubstituted on the same carbon atom, as in the case of CF_3 or CH_2CF_3 , or at different positions, as in the case of $\text{CH}(\text{Cl})\text{-CH=CH-CHCl}_2$. Polysubstitution can be carried out with the same or with different substituents, such as, for example, in the case of $\text{CH}(\text{OH})\text{-CH=CH-CHCl}_2$.

[0036] More preferably, R^1 and R^2 , independently of one another, are branched, unsubstituted $\text{C}_{14}\text{-C}_{40}$ alkyl or R^1 is branched, unsubstituted $\text{C}_{8}\text{-C}_{40}$ alkyl and R^2 is $\text{C}_{35}\text{-C}_{200}$ polyisobutene.

[0037] Even more preferably R^1 and R^2 are, independently of one another, selected from the group consisting of isotetradecyl, isopentadecyl, isohexadecyl, isoheptadecyl, isoctadecyl, isononadecyl, isoeicosyl, isoheneicosyl, isodocosyl, isotricosyl, isotetracosyl, isopentacosyl, isohexacosyl, isoheptacosyl, isoctacosyl, isononacosyl, isotriacontyl, 45 isohentriacontyl, isodotriacontyl, isotritriacontyl, isotetracontyl, isopentatriacontyl, isohexatriacontyl, isoheptatriac-
ontyl, isoctatriacontyl, isononatriacontyl and isotetracontyl or represented by formula (II)



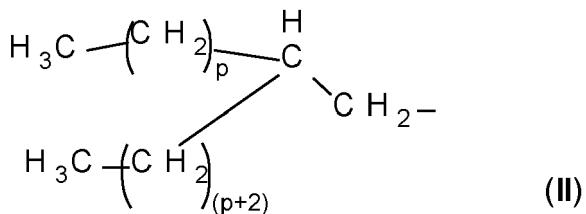
where p may be 4, 5, 6, 7, 8, 9, 10 or 11

or

R^1 is selected from the group consisting of isoctyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl, isotetradecyl,

isopentadecyl, isohexadecyl, isoheptadecyl, isoctadecyl, isononadecyl, isoeicosyl, isoheneicosyl, isodocosyl, isotriocosyl, isotetracosyl, isopentacosyl, isohexacosyl, isoheptacosyl, isoctacosyl, isononacosyl, isotriacetyl, isohentriacetyl, isodotriacetyl, isotriacetyl, isotetratriacetyl, isopentatriacetyl, isohexatriacetyl, isoheptatriacetyl, isoctatriacetyl, isononatriacetyl and isotetraacetyl or represented by formula (II)

5

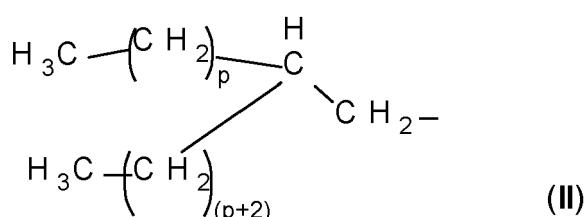


mixture of the 2,4 and 2,6 isomers of toluene diisocyanate.

[0042] In case a mixture of diisocyanate, toluene 2,4-diisocyanate and toluene 2,6-diisocyanate is used, the resulting diurea compounds of general formula (I) are also obtained as mixtures.

[0043] Preferably, the lubricant compositions contain mixtures of compounds of general formula (I) prepared by reacting a mixture of toluene 2,4-diisocyanate and toluene 2,6-diisocyanate with a monoamine.

[0044] Monoamine can be selected from *n*-octylamine, *n*-nonylamine, *n*-decylamine, *n*-undecylamine, *n*-dodecylamine, *n*-tridecylamine, *n*-tetradecylamine, *n*-pentadecylamine, *n*-hexadecylamine, *n*-heptadecylamine, *n*-octadecylamine, *n*-nonadecylamine, *n*-eicosylamine, *n*-heneicosylamine, *n*-docosylamine, *n*-tricosylamine, *n*-tetracosylamine, *n*-pentacosylamine, *n*-hexacosylamine, *n*-heptacosylamine, *n*-octacosylamine, *n*-nonacosylamine, *n*-triacontylamine, *n*-hentriacontylamine, *n*-dotriacontylamine, *n*-tritriacontylamine, *n*-tetratriacontylamine, *n*-pentatriacontylamine, *n*-hexatriacontylamine, *n*-heptatriacontylamine, *n*-octatriacontylamine, *n*-nonatriacontylamine, *n*-tetracontylamine, *iso*octylamine, *iso*nonylamine, *iso*decylamine, *iso*undecylamine, *iso*dodecylamine, *iso*tridecylamine, *iso*tetradecylamine, *iso*pentadecylamine, *iso*hexadecylamine, *iso*heptadecylamine, *iso*octadecylamine, *iso*nonaicosylamine, *iso*eicosylamine, *iso*heneicosylamine, *iso*docosylamine, *iso*tricosylamine, *iso*pentacosylamine, *iso*hexacosylamine, *iso*heptacosylamine, *iso*octacosylamine, *iso*nonacosylamine, *iso*triacontylamine, *iso*hentriacontylamine, *iso*dotriacontylamine, *iso*tritriacontylamine, *iso*tetratriacontylamine, *iso*pentatriacontylamine, *iso*hexatriacontylamine, *iso*heptatriacontylamine, *iso*octatriacontylamine, *iso*nonatriacontylamine, *iso*tetracontylamine and polyisobutene amine or radical derived from guerbet alcohol having the general formula II,



where p is preferably 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11.

[0045] The polyisobutene amine (PIBA) is obtained by the hydroformylation of polyisobutene with a number-average molecular weight of 1000 g/mol and a fraction of more than 70% vinylidene bonds and its subsequent amination. Processes for the synthesis of polyisobutene amine are known in principle to those skilled in the art, for example from WO 2004/087808.

[0046] Number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity of polyisobutylene are determined by gel permeation chromatography (GPC): Eluent THF, column temperature 35°C, column material Prgel 10 μ m, length 30 cm, diameter 7.5 mm, guard column length 5 cm diameter 7.5 mm (Supplier Agilent). For calibration polyisobutylene standards (available from Polymer Standard Service) with $M = 340$ to $M = 801000$ are used. Flow 1 mL/min, concentration 2 mg/mL, injection 100 μ L. Detector: DRI 1100 series (Agilent).

[0047] The polyisobutene has a carbon atom number in the range of C_{35} to C_{200} , preferably in the range of C_{50} to C_{100} , more preferably in the range of C_{60} to C_{80} .

[0048] The monoamines are reacted with the diisocyanates in an organic solvent (F. Lortie, Langmuir 2002, 18, 7218). The resulting product is separated from the organic solvent and then dissolved in base oil to prepare inventive compositions.

[0049] In a preferred embodiment, the at least one compound of general formula (I) has a number average molecular weight in the range of ≥ 400 g/mol to ≤ 3000 g/mol, more preferably in the range of ≥ 500 g/mol to ≤ 2600 g/mol, even more preferably in the range of ≥ 600 g/mol to ≤ 2400 g/mol and most preferably in the range of ≥ 700 g/mol to ≤ 2200 g/mol, as determined by gel permeation chromatography.

[0050] In another aspect the presently claimed invention is directed to a composition comprising ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I) as defined above, more preferably in the range of ≥ 0.2 to ≤ 18 % by weight, even more preferably in the range of ≥ 1.0 to ≤ 5.0 % by weight or ≥ 6.0 to ≤ 10.0 % by weight or ≥ 10.0 to ≤ 14.0 % by weight or ≥ 14.0 to ≤ 18.0 % by weight and most preferably in the range of ≥ 1.0 to ≤ 3.0 % by weight or ≥ 3.0 to ≤ 5.0 % by weight or ≥ 5.0 to ≤ 7.0 % by weight or ≥ 7.0 to ≤ 9.0 % by weight or ≥ 9.0 to ≤ 11.0 % by weight or ≥ 11.0 to ≤ 13.0 % by weight or ≥ 13.0 to ≤ 15.0 % by weight or ≥ 15.0 to ≤ 17.0 % by weight or ≥ 17.0 to ≤ 19.0 % by weight.

[0051] The specific embodiments of the at least one compound of general formula (I) as defined above also apply to at least one compound of general formula (I) which is incorporated into a composition, in particular into a lubricant composition or a grease.

Base oil

[0052] Preferably the lubricant composition comprises ≥ 80 to ≤ 99.9 % by weight, of at least one base oil, more preferably ≥ 80 to ≤ 95 % by weight of at least one base oil, in each case related to the overall weight of the lubricant composition.

[0053] The base oil is selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils.

[0054] Definitions for the base oils according to the present invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base oils/stocks as follows:

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

b) Group II base oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120, using the test methods specified in the following table.

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

Analytical Methods for Base Stock:

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulfur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

d) Group IV base oils contain polyalphaolefins. Synthetic lower viscosity fluids suitable for the present invention include the polyalphaolefins (PAOs) and the synthetic oils from the hydrocracking or hydro-isomerization of Fischer Tropsch high boiling fractions including waxes. These are both base oils comprised of saturates with low impurity levels consistent with their synthetic origin. The hydro-isomerized Fischer Tropsch waxes are highly suitable base oils, comprising saturated components of iso-paraffinic character (resulting from the isomerization of the predominantly n-paraffins of the Fischer Tropsch waxes) which give a good blend of high viscosity index and low pour point. Processes for the hydro-isomerization of Fischer Tropsch waxes are described in U.S. Patents 5,362,378; 5,565,086; 5,246,566 and 5,135,638, as well as EP 710710, EP 321302 and EP 321304.

[0055] Polyalphaolefins suitable for the lubricant compositions according to the present invention, include known PAO materials which typically comprise relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include but are not limited to C₂ to about C₃₂ alphaolefins with the C₈ to about C₁₆ alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene, and poly-1-dodecene, although the dimers of higher olefins in the range of C₁₄ to C₁₈ provide low viscosity base stocks.

[0056] Terms like PAO 2, PAO 4, PAO 6 or PAO 8 are commonly used specifications for different classes of polyalphaolefins characterized by their respective viscosity. For instance, PAO 2 refers to the class of polyalphaolefins which typically has viscosity in the range of 2 mm²/s at 100°C. A variety of commercially available compositions are available for these specifications.

[0057] Low viscosity PAO fluids suitable for the lubricant compositions according to the present invention, may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example, the methods disclosed by U.S. Patents 3,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patents: 3,742,082 (Brennan); 3,769,363 (Brennan); 3,876,720 (Heilman); 4,239,930 (Allphin); 4,367,352 (Watts); 4,413,156 (Watts); 4,434,308 (Larkin); 4,910,355 (Shubkin); 4,956,122 (Watts); and 5,068,487 (Theriot).

[0058] For the present invention, PAO 2 and PAO 4 are the preferred polyalphaolefins.

e) Group V base oils contain any base stocks not described by Groups I to IV. Examples of Group V base oils include carboxylic acid esters, alkyl naphthalenes, alkylene oxide polymers, silicone oils, and phosphate esters.

[0059] Synthetic base oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof.

[0060] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic base oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of polyethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ Oxo acid diester of tetraethylene glycol.

[0061] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic base oils; such base oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl) disiloxane and poly(methylphenyl) siloxanes. Other synthetic base oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0062] Preferably the carboxylic acid esters are monoesters, diesters, triesters or polyesters, more preferably esters of monohydric alcohols and monobasic acids, esters of dihydric and/or polyhydric alcohols and monobasic acids and esters of monohydric alcohols and dibasic acids.

[0063] Monohydric alcohols that are usually employed comprise C₁-C₂₄, preferably C₁-C₁₂ and more preferably C₁-C₈ monohydric alcohols, and such alcohols may be straight-chain or branched, and either saturated or unsaturated. As specific examples of C₁-C₂₄ alcohols there may be mentioned methanol, ethanol, straight-chain or branched propanol, straight-chain or branched butanol, straight-chain or branched pentanol, straight-chain or branched hexanol, straight-chain or branched heptanol, straight-chain or branched octanol, straight-chain or branched nonanol, straight-chain or branched decanol, straight-chain or branched undecanol, straight-chain or branched dodecanol, straight-chain or branched tridecanol, straight-chain or branched tetradecanol, straight-chain or branched pentadecanol, straight-chain or branched hexadecanol, straight-chain or branched heptadecanol, straight-chain or branched octadecanol, straight-chain or branched nonadecanol, straight-chain or branched eicosanol, straight-chain or branched heneicosanol, straight-chain or branched tricosanol, straight-chain or branched tetracosanol, and mixtures thereof.

[0064] Dihydric alcohols that are usually employed comprise ethylene glycol, diethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, 1,3-propanediol, 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,2-propanediol, 2-methyl-1,3-propanediol, 1,2-pentanediol, 1,3-pentanediol, 1,4-pentanediol, 1,5-pentanediol, neopentyl glycol, and mixtures thereof.

[0065] Polyhydric alcohols that are usually employed comprise trimethylolpropane, ditrimethylolethane, trimethylolpropane, ditrimethylolpropane, glycerin, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol.

[0066] Monobasic acids that are usually employed comprise C₂-C₂₄ fatty acids, and the fatty acids may be straight-chain or branched and either saturated or unsaturated. As specific examples there may be mentioned saturated fatty acids such as acetic acid, propionic acid, straight-chain or branched butanoic acid, straight-chain or branched pentanoic acid, straight-chain or branched hexanoic acid, straight-chain or branched heptanoic acid, straight-chain or branched octanoic acid, straight-chain or branched nonanoic acid, straight-chain or branched decanoic acid, straight-chain or branched undecanoic acid, straight-chain or branched dodecanoic acid, straight-chain or branched tridecanoic acid, straight-chain or branched tetradecanoic acid, straight-chain or branched pentadecanoic acid, straight-chain or branched hexadecanoic acid, straight-chain or branched heptadecanoic acid, straight-chain or branched octadecanoic acid, straight-chain or branched hydroxyoctadecanoic acid, straight-chain or branched nonadecanoic acid, straight-chain or branched eicosanoic acid, straight-chain or branched heneicosanoic acid, straight-chain or branched docosanoic acid, straight-chain or branched tricosanoic acid and straight-chain or branched tetracosanoic acid; unsaturated fatty acids such as acrylic acid, straight-chain or branched butenoic acid, straight-chain or branched pentenoic acid, straight-chain or branched hexenoic acid, straight-chain or branched heptenoic acid, straight-chain or branched octenoic acid, straight-chain or branched nonenoic acid, straight-chain or branched decenoic acid, straight-chain or branched undecenoic acid, straight-chain or branched dodecenoic acid, straight-chain or branched tridecenoic acid, straight-chain or branched tetradecenoic acid, straight-chain or branched pentadecenoic acid, straight-chain or branched hexadecenoic acid, straight-chain or branched heptadecenoic acid, straight-chain or branched octadecenoic acid, straight-chain or branched hydroxyoctadecenoic acid, straight-chain or branched nonadecenoic acid, straight-chain or branched eicosenoic acid,

straight-chain or branched heneicosenoic acid, straight-chain or branched docosenoic acid, straight-chain or branched tricosenoic acid and straight-chain or branched tetracosenoic acid; and mixtures thereof.

[0067] Dibasic acids that are usually employed comprise C₂-C₁₆ dibasic acids. Such C₂-C₁₆ dibasic acids may be straight-chain or branched, and either saturated or unsaturated. As specific examples there may be mentioned ethanedioic acid, propanedioic acid, straight-chain or branched butanedioic acid, straight-chain or branched pentanedioic acid, straight-chain or branched hexanedioic acid, straight-chain or branched heptanedioic acid, straight-chain or branched octanedioic acid, straight-chain or branched nonanedioic acid, straight-chain or branched decanedioic acid, straight-chain or branched undecanedioic acid, straight-chain or branched dodecanedioic acid, straight-chain or branched tridecanedioic acid, straight-chain or branched tetradecanedioic acid, straight-chain or branched heptadecanedioic acid, straight-chain or branched hexadecanedioic acid, straight-chain or branched hexenedioic acid, straight-chain or branched heptenedioic acid, straight-chain or branched octenedioic acid, straight-chain or branched nonenedioic acid, straight-chain or branched decenedioic acid, straight-chain or branched undecenedioic acid, straight-chain or branched dodecenedioic acid, straight-chain or branched tridecenedioic acid, straight-chain or branched tetradecenedioic acid, straight-chain or branched heptadecenedioic acid, straight-chain or branched hexadecenedioic acid, and mixtures thereof.

[0068] The carboxylic acid esters may be total carboxylic acid esters wherein all of the hydroxyl groups of the dihydric alcohol and/or polyhydric alcohols are esterified, or they may be partial carboxylic acid esters wherein a portion of the hydroxyl groups remain as hydroxyl groups without esterification. The carboxylic acid esters may also be total carboxylic acid esters wherein all of the carboxyl groups of the polybasic acid are esterified, or they may be partial carboxylic acid esters wherein a portion of the carboxyl groups remain as carboxyl groups without esterification.

[0069] Preferably the carboxylic acid ester is selected from the group consisting of 2-ethylhexyl stearate and di-(2-propylheptyl) adipate.

[0070] In another preferred embodiment, the base oil is selected from the group consisting of group III mineral oil, group IV polyalphaolefins (PAO) and group V esters.

25 Additives

[0071] Preferably the lubricant composition comprises ≥ 0.0 to ≤ 20 % by weight of at least one additive component, more preferably ≥ 0.1 to ≤ 20 % by weight of at least one additive component, more preferably ≥ 0.1 to ≤ 10 % by weight of at least one additive component, in each case related to the overall weight of the lubricant composition.

[0072] The lubricant composition according to the present invention may further comprise an additive component. In a preferred embodiment, the additive component is selected from the group consisting of antioxidants, dispersants, foam inhibitors, demulsifiers, seal swelling agents, friction reducers, anti-wear agents, detergents, corrosion inhibitors, extreme pressure agents, metal deactivators, rust inhibitors, pour point depressants and mixtures thereof.

[0073] The additive component as used in the present invention also includes an additive package and/or performance additives.

[0074] The additive package as used in the present invention as well as the compounds relating to performance additives are considered mixtures of additives that are typically used in lubricant compositions in limited amounts for mechanically, physically or chemically stabilizing the lubricant compositions while special performance characteristics can be further established by the individual or combined presence of such selected additives.

[0075] Additive packages are separately defined in the present invention since a variety of such additive packages are commercially available and typically used in lubricant compositions. One such preferred additive package that is commercially available is marketed under the name Anglamol6004J®.

[0076] However, the individual components contained in the additive packages and/or the compounds further defined in the present invention as so-called performance additives include a larger number of different types of additives including dispersants, metal deactivators, detergents, extreme pressure agents (typically boron- and/or sulfur- and/or phosphorus-containing), anti-wear agents, antioxidants (such as hindered phenols, aminic antioxidants or molybdenum compounds), corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, friction modifiers and mixtures thereof.

[0077] The additive component as the sum of all additives contained in the lubricant compositions according to the present invention also including all additives contained in an additive package or added separately is present in the lubricant compositions of the present invention in an amount of 0.0 to 20 wt. %, preferably 0.1 to 10 wt. %.

[0078] Extreme pressure agents include compounds containing boron and/or sulfur and/or phosphorus. The extreme pressure agent may be present in the lubricant compositions at 0 % by weight to 15 % by weight, or 0.05 % by weight to 10 % by weight, or 0.1 % by weight to 8 % by weight of the lubricant composition.

[0079] In one embodiment according to the present invention, the extreme pressure agent is a sulfur-containing compound. In one embodiment, the sulfur-containing compound may be a sulfurised olefin, a polysulfide, or mixtures thereof. Examples of the sulfurised olefin include a sulfurised olefin derived from propylene, isobutylene, pentene; an organic sulfide and/or polysulfide including benzylsulfide; bis-(chlorobenzyl) disulfide; dibutyl tetrasulfide; di-tertiary butyl

polysulfide; and sulfurised methyl ester of oleic acid, a sulfurised alkylphenol, a sulfurised dipentene, a sulfurised terpene, a sulfurised Diels-Alder adduct, an alkyl sulphenyl N'N- dialkyl dithiocarbamates; or mixtures thereof.

[0080] In one embodiment the sulfurised olefin includes a sulfurised olefin derived from propylene, isobutylene, pentene or mixtures thereof.

[0081] In one embodiment according to the present invention, the extreme pressure agent sulfur-containing compound includes a dimercaptothiadiazole or derivative, or mixtures thereof. Examples of the dimercaptothiadiazole include compounds such as 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof. The oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically form by forming a sulfur-sulfur bond between 2,5-dimercapto-1,3,4-thiadiazole units to form derivatives or oligomers of two or more of said thiadiazole units. Suitable 2,5-dimercapto-1,3,4-thiadiazole derived compounds include for example 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole or 2-tert-nonyldithio-5-mercaptop-1,3,4-thiadiazole. The number of carbon atoms on the hydrocarbyl substituents of the hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically include 1 to 30, or 2 to 20, or 3 to 16.

[0082] In one embodiment, the dimercaptothiadiazole may be a thiadiazole-functionalised dispersant. A detailed description of the thiadiazole-functionalised dispersant is described in paragraphs [0028] to [0052] of International Publication WO 2008/014315.

[0083] The thiadiazole-functionalised dispersant may be prepared by a method including heating, reacting or complexing a thiadiazole compound with a dispersant substrate. The thiadiazole compound may be covalently bonded, salted, complexed or otherwise solubilized with a dispersant, or mixtures thereof.

[0084] The relative amounts of the dispersant substrate and the thiadiazole used to prepare the thiadiazole-functionalised dispersant may vary. In one embodiment the thiadiazole compound is present at 0.1 to 10 parts by weight relative to 100 parts by weight of the dispersant substrate. In different embodiments the thiadiazole compound is present at greater than 0.1 to 9, or greater than 0.1 to less than 5, or 0.2 to less than 5: to 100 parts by weight of the dispersant substrate. The relative amounts of the thiadiazole compound to the dispersant substrate may also be expressed as (0.1-10):100, or (>0.1-9):100, (such as (>0.5-9):100), or (0.1 to less than 5): 100, or (0.2 to less than 5): 100.

[0085] In one embodiment the dispersant substrate is present at 0.1 to 10 parts by weight relative to 1 part by weight of the thiadiazole compound. In different embodiments the dispersant substrate is present at greater than 0.1 to 9, or greater than 0.1 to less than 5, or about 0.2 to less than 5: to 1 part by weight of the thiadiazole compound. The relative amounts of the dispersant substrate to the thiadiazole compound may also be expressed as (0.1-10):1, or (>0.1-9):1, (such as (>0.5-9): 1), or (0.1 to less than 5): 1, or (0.2 to less than 5): 1.

[0086] The thiadiazole-functionalised dispersant may be derived from a substrate that includes a succinimide dispersant (for example, N-substituted long chain alkenyl succinimides, typically a polyisobutylene succinimide), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant, a polyetheramine dispersant, a viscosity modifier containing dispersant functionality (for example polymeric viscosity index modifiers containing dispersant functionality), or mixtures thereof. In one embodiment the dispersant substrate includes a succinimide dispersant, an ester-containing dispersant or a Mannich dispersant.

[0087] In one embodiment according to the present invention, the extreme pressure agent includes a boron-containing compound. The boron-containing compound includes a borate ester (which in some embodiments may also be referred to as a borated epoxide), a borated alcohol, a borated dispersant, a borated phospholipid or mixtures thereof. In one embodiment the boron-containing compound may be a borate ester or a borated alcohol.

[0088] The borate ester may be prepared by the reaction of a boron compound and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. The alcohols include dihydric alcohols, trihydric alcohols or higher alcohols, with the proviso for one embodiment that hydroxyl groups are on adjacent carbon atoms, i.e., vicinal.

[0089] Boron compounds suitable for preparing the borate ester include the various forms selected from the group consisting of boric acid (including metaboric acid, orthoboric acid and tetraboric acid), boric oxide, boron trioxide and alkyl borates. The borate ester may also be prepared from boron halides.

[0090] In one embodiment suitable borate ester compounds include tripropyl borate, tributyl borate, tripentyl borate, trihexyl borate, triheptyl borate, trioctyl borate, trinonyl borate and tridecyl borate. In one embodiment the borate ester compounds include tributyl borate, tri-2-ethylhexyl borate or mixtures thereof.

[0091] In one embodiment, the boron-containing compound is a borated dispersant, typically derived from an N-substituted long chain alkenyl succinimide. In one embodiment the borated dispersant includes a polyisobutylene succinimide. Borated dispersants are described in more detail in US Patents 3,087,936 and Patent 3,254,025.

[0092] In one embodiment the borated dispersant may be used in combination with a sulfur-containing compound or a borate ester.

[0093] In one embodiment the extreme pressure agent is other than a borated dispersant.

[0094] The number average molecular weight Mn (GPC; kg/mol) of the hydrocarbon from which the long chain alkenyl

group was derived includes ranges of 350 to 5000, or 500 to 3000, or 550 to 1500. The long chain alkenyl group may have a number average molecular weight M_n of 550, or 750, or 950 to 1000.

[0095] The N-substituted long chain alkenyl succinimides are borated using a variety of agents including boric acid (for example, metaboric acid, orthoboric acid and tetraboric acid), boric oxide, boron trioxide, and alkyl borates. In one embodiment the borating agent is boric acid which may be used alone or in combination with other borating agents.

[0096] The borated dispersant may be prepared by blending the boron compound and the N-substituted long chain alkenyl succinimides and heating them at a suitable temperature, such as, 80 °C to 250 °C, or 90 °C to 230 °C, or 100 °C to 210 °C, until the desired reaction has occurred. The molar ratio of the boron compounds to the N-substituted long chain alkenyl succinimides may have ranges including 10:1 to 1:4, or 4:1 to 1:3; or the molar ratio of the boron compounds to the N-substituted long chain alkenyl succinimides may be 1:2. Alternatively, the ratio of moles B : moles N (that is, atoms of B : atoms of N) in the borated dispersant may be 0.25:1 to 10:1 or 0.33:1 to 4:1 or 0.2:1 to 1.5:1, or 0.25:1 to 1.3:1 or 0.8:1 to 1.2:1 or about 0.5:1 An inert liquid may be used in performing the reaction. The liquid may include toluene, xylene, chlorobenzene, dimethylformamide or mixtures thereof.

[0097] In one embodiment, the additive component in the lubricant composition according to the present invention further includes a borated phospholipid. The borated phospholipid may be derived from boronation of a phospholipid (for example boronation may be carried out with boric acid). Phospholipids and lecithins are described in detail in Encyclopedia of Chemical Technology, Kirk and Othmer, 3rd Edition, in "Fats and Fatty Oils", Volume 9, pages 795-831 and in "Lecithins", Volume 14, pages 250-269.

[0098] The phospholipid may be any lipid containing a phosphoric acid, such as lecithin or cephalin, or derivatives thereof. Examples of phospholipids include phosphatidylcholine, phosphati-dylserine, phosphatidylinositol, phosphatidyl-ethanolamine, phosphatidic acid and mixtures thereof. The phospholipids may be glycerophospholipids, glycerol derivatives of the above list of phospholipids. Typically, the glycerophospholipids have one or two acyl, alkyl or alkenyl groups on a glycerol residue. The alkyl or alkenyl groups may contain 8 to 30, or 8 to 25, or 12 to 24 carbon atoms. Examples of suitable alkyl or alkenyl groups include octyl, dodecyl, hexadecyl, octadecyl, docosanyl, octenyl, dodecenyl, hexadecenyl and octadecenyl.

[0099] Phospholipids may be prepared synthetically or derived from natural sources. Synthetic phospholipids may be prepared by methods known to those in the art. Naturally derived phospholipids are often extracted by procedures known to those in the art. Phospholipids may be derived from animal or vegetable sources. A useful phospholipid is derived from sunflower seeds. The phospholipid typically contains 35 % to 60 % phosphatidylcholine, 20 % to 35 % phosphati-dylinositol, 1 % to 25 % phosphatidic acid, and 10 % to 25 % phosphatidylethanolamine, wherein the percentages are by weight based on the total phospholipids. The fatty acid content may be 20 % by weight to 30 % by weight palmitic acid, 2 % by weight to 10 % by weight stearic acid, 15 % by weight to 25 % by weight oleic acid, and 40 % by weight to 55 % by weight linoleic acid.

[0100] In another embodiment, the performance additive in the lubricant compositions according to the present invention may include a friction modifier. A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricant compositions of the present invention if desired. Friction modifiers may include metal-containing compounds or materials as well as ashless compounds or materials, or mixtures thereof. Metal-containing friction modifiers may include metal salts or metal-ligand complexes where the metals may include alkali, alkaline earth, or transition group metals. Such metal-containing friction modifiers may also have low-ash characteristics. Transition metals may include Mo, Sb, Sn, Fe, Cu, Zn, and others.

[0101] Ligands may include hydrocarbyl derivative of alcohols, polyols, glycerols, partial ester glycerols, thiols, carboxylates, carbamates, thiocarbamates, dithiocarbamates, phosphates, thiophosphates, dithiophosphates, amides, imides, amines, thiazoles, thiadiazoles, dithiazoles, diazoles, triazoles, and other polar molecular functional groups containing effective amounts of O, N, S, or P, individually or in combination. In particular, Mo-containing compounds can be particularly effective such as for example Mo-dithiocarbamates, Mo(DTC), Mo-dithiophosphates, Mo(DTP), Mo-amines, Mo (Am), Mo-alcoholates, Mo-alcohol-amides, and the like.

[0102] Ashless friction modifiers may also include lubricant materials that contain effective amounts of polar groups, for example, hydroxyl-containing hydrocarbyl base oils, glycerides, partial glycerides, glyceride derivatives, and the like. Polar groups in friction modifiers may include hydrocarbyl groups containing effective amounts of O, N, S, or P, individually or in combination. Other friction modifiers that may be particularly effective include, for example, salts (both ash-containing and ashless derivatives) of fatty acids, fatty alcohols, fatty amides, fatty esters, hydroxyl-containing carboxylates, and comparable synthetic long-chain hydrocarbyl acids, alcohols, amides, esters, hydroxy carboxylates, and the like. In some instances fatty organic acids, fatty amines, and sulfurized fatty acids may be used as suitable friction modifiers.

[0103] In one embodiment, the performance additive in the lubricant compositions according to the present invention may include phosphorus- or sulfur- containing anti-wear agents other than compounds described as an extreme pressure

agent of the amine salt of a phosphoric acid ester described above. Examples of the anti-wear agent may include a non-ionic phosphorus compound (typically compounds having phosphorus atoms with an oxidation state of +3 or +5), a metal dialkyldithiophosphate (typically zinc dialkyldithiophosphates), amine dithiophosphate, ashless dithiophosphates and a metal mono- or di-alkylphosphate (typically zinc phosphates), or mixtures thereof.

5 [0104] The non-ionic phosphorus compound includes a phosphite ester, a phosphate ester, or mixtures thereof.

[0105] In one embodiment, the performance additive in the lubricant composition according to the present invention may further include at least one antioxidant. Antioxidants retard the oxidative degradation of base stocks during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions.

10 [0106] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C₆₊ alkyl groups and the alkylene coupled derivatives 15 of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for 20 example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant invention. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4'-bis(2,6-di-t-butyl phenol) and 4,4'-methylene-bis(2,6-di-t-butyl phenol).

25 [0107] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula R⁸R⁹R¹⁰N, where R⁸ is an aliphatic, aromatic or substituted aromatic group, R⁹ is an aromatic or a substituted aromatic group, and R¹⁰ is H, alkyl, aryl or R¹¹S(O)_xR¹², where R¹¹ is an alkylene, alkenylene, or aralkylene group, R¹² is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R⁸ may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R⁸ and R⁹ are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as 30 naphthyl. Aromatic groups R⁸ and R⁹ may be joined together with other groups such as S.

35 [0108] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alpha-naphthylamine; and p-octylphenyl-alpha-naphthylamine. Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

40 [0109] In one embodiment, the performance additive in the lubricant compositions according to the present invention further includes a dispersant. The dispersant may be a succinimide dispersant (for example N-substituted long chain alkenyl succinimides), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant or a polyetheramine dispersant.

45 [0110] In one embodiment the succinimide dispersant includes a polyisobutylene-substituted succinimide, wherein the polyisobutylene from which the dispersant is derived may have a number average molecular weight of 400 to 5000, or 950 to 1600. Succinimide dispersants and their methods of preparation are more fully described in U.S. Patents 4,234,435 and 3,172,892. Suitable ester-containing dispersants are typically high molecular weight esters. These materials are described in more detail in U.S. Patent 3,381,022.

50 [0111] In one embodiment the dispersant includes a borated dispersant. Typically the borated dispersant includes a succinimide dispersant including a polyisobutylene succinimide, wherein the polyisobutylene from which the dispersant is derived may have a number average molecular weight of 400 to 5000. Borated dispersants are described in more detail above within the extreme pressure agent description.

55 [0112] Dispersant viscosity modifiers (often referred to as DVMs) are considered additives in the context of the present invention due to their additional functionalization and are therefore not considered viscosity improving agents according to the present invention. Dispersant viscosity modifiers include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of maleic anhydride and an amine, a polymethacrylate functionalised with an amine, or esterified styrene maleic anhydride copolymers reacted with an amine.

[0113] As another type of performance additives, corrosion inhibitors can be described as any materials (additives,

functionalized fluids, etc.) that form a protective film on a surface that prevents corrosion agents from reacting or attacking that surface with a resulting loss of surface material. Protective films may be absorbed on the surface or chemically bonded to the surface. Protective films may be constituted from mono-molecular species, oligomeric species, polymeric species, or mixtures thereof. Protective films may derive from the intact corrosion inhibitors, from their combination products, or their degradation products, or mixtures thereof. Surfaces that may benefit from the action of corrosion inhibitors may include metals and their alloys (both ferrous and non-ferrous types) and non-metals.

5 [0114] Corrosion inhibitors may include various oxygen-, nitrogen-, sulfur-, and phosphorus-containing materials, and may include metal-containing compounds (salts, organometallics, etc.) and nonmetal-containing or ashless materials. Corrosion inhibitors may include, but are not limited to, additive types such as, for example, hydrocarbyl-, aryl-, alkyl-, 10 arylalkyl-, and alkylaryl-versions of detergents (neutral, overbased), sulfonates, phenates, salicylates, alcoholates, carboxylates, salixarates, phosphites, phosphates, thiophosphates, amines, amine salts, amine phosphoric acid salts, amine sulfonic acid salts, alkoxyLATED amines, etheramines, polyetheramines, amides, imides, azoles, diazoles, triazoles, benzotriazoles, benzothiadoles, mercaptobenzothiazoles, tolyltriazoles (TTZ-type), heterocyclic amines, heterocyclic sulfides, thiazoles, thiadiazoles, mercaptothiadiazoles, dimercaptothiadiazoles (DMTD-type), imidazoles, benzimidazoles, 15 dithiobenzimidazoles, imidazolines, oxazolines, Mannich reactions products, glycidyl ethers, anhydrides, carbamates, thiocarbamates, dithiocarbamates, polyglycols, etc., or mixtures thereof.

[0115] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricant composition. Suitable corrosion inhibitors include thiadiazoles. Aromatic triazoles, such as tolyltriazole, are suitable corrosion inhibitors for non-ferrous metals, such as copper.

20 [0116] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, thiadiazoles or 2-alkyldithiobenzothiazoles.

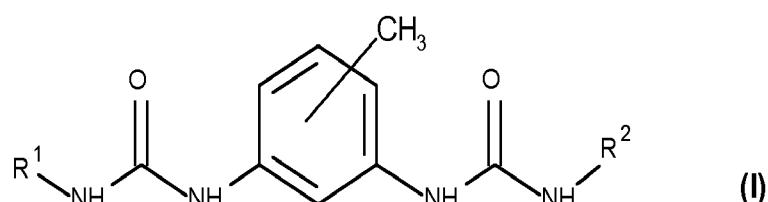
[0117] 25 Foam inhibitors may also advantageously be added as a performance additive to the lubricant compositions according to the present invention. These agents retard the formation of stable foams. Silicones and organic polymers are typical foam inhibitors. For example, polysiloxanes, such as silicon oil, or polydimethylsiloxane, provide foam inhibiting properties. Further foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexyl acrylate and optionally vinyl acetate.

[0118] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0119] As pour point depressants, esters of maleic anhydride-styrene, or polyacrylamides are included.

[0120] 30 As a further performance additive to be used in the lubricant compositions according to the present invention, seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricant compositions include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may preferably be used in an amount of 0.01 to 3 % by weight, more preferably 0.01 to 2 % by weight of the 35 total amount of the lubricant composition.

[0121] 40 In another preferred embodiment the presently claimed invention is directed to the use of at least a compound of general formula (I) as thickening agent



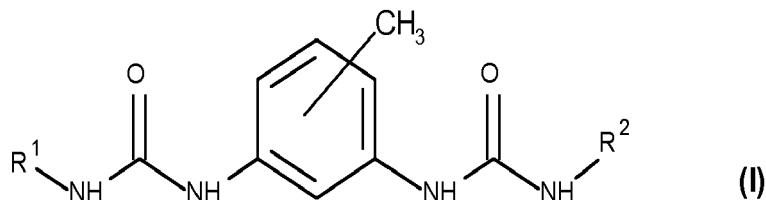
wherein

50 R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl, or

R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11 .

[0122] 55 In a preferred embodiment, the presently claimed invention is directed to a composition comprising

a) ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I)



10 wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁₄-C₄₀-alkyl, or

15 R¹ is linear or branched, substituted or unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

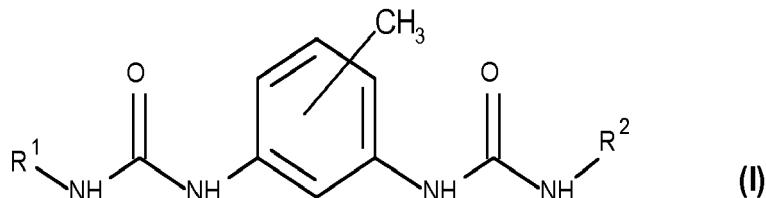
b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

c) ≥ 0.0 to ≤ 20 % by weight of at least one additive component,

20 whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11.

25 [0123] In another preferred embodiment, the presently claimed invention is directed to a composition comprising

a) ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I)



35 wherein

R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl, or

R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

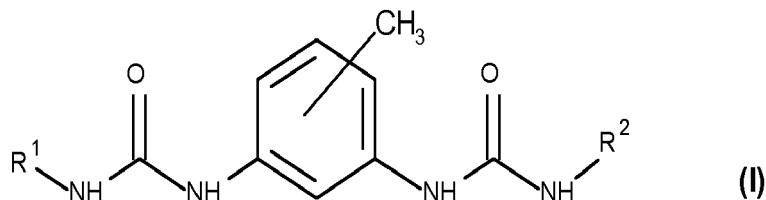
40 b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

45 c) ≥ 0.0 to ≤ 20 % by weight of at least one additive component,

50 whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11.

[0124] In another preferred embodiment, the presently claimed invention is directed to a composition comprising

a) ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I)



10 wherein

R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl,

or

R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

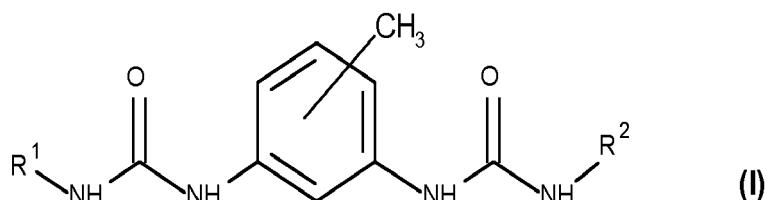
15 b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

c) ≥ 0.1 to ≤ 20 % by weight of at least one additive component,

20 whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11.

[0125] In another preferred embodiment, the presently claimed invention is directed to a composition comprising

25 a) ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I)



35 wherein

R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl,

or

R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

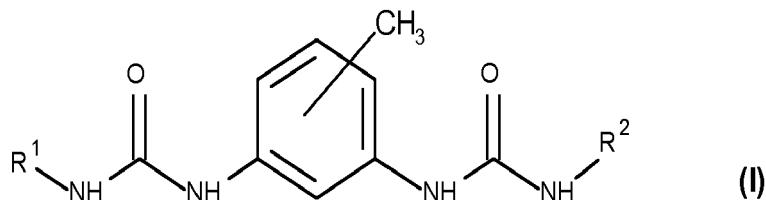
40 b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

c) ≥ 0.0 to ≤ 20 % by weight of at least one additive component,

45 whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 9.

[0126] In another preferred embodiment, the presently claimed invention is directed to a composition comprising of

50 a) ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I)



10 wherein

R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl,

or

R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

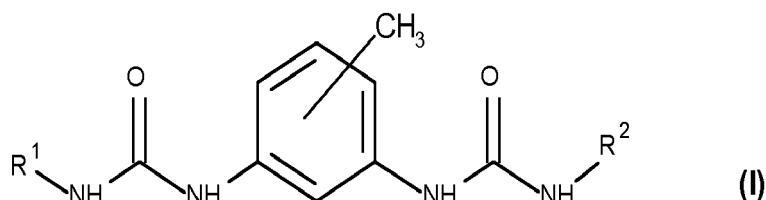
15 b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

c) ≥ 0.1 to ≤ 10 % by weight of at least one additive component,

20 whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11.

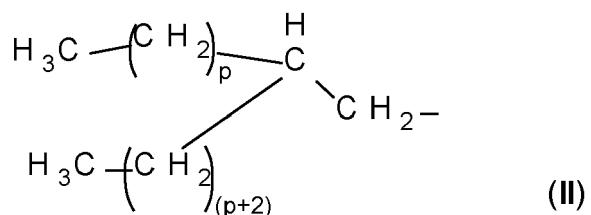
[0127] In another preferred embodiment, the presently claimed invention is directed to a composition consisting of

25 a) ≥ 0.2 to ≤ 20 %, preferably ≥ 0.2 to ≤ 2.0 %, by weight of at least one compound of general formula (I)



35 wherein

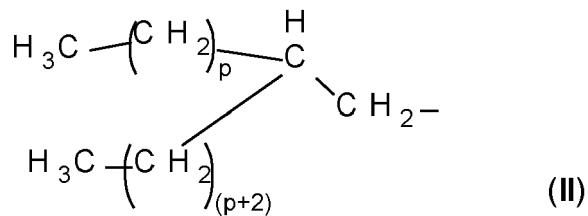
R¹ and R² are, independently of one another, selected from the group consisting of isotetradecyl, isopentadecyl, isohexadecyl, isoheptadecyl, isoctadecyl, isononadecyl, isoeicosyl, isoheneicosyl, isodocosyl, isotricosyl, isotetraacosyl, isopentacosyl, isohexacosyl, isoheptacosyl, isoctacosyl, isononacosyl, isotriacontyl, isohentriacontyl, isodotriacontyl, isotritriacontyl, isotetratriacontyl, isopentatriacontyl, isohexatriacontyl, isoheptatriacontyl, isoctatriac-40 ontyl, isononatriacontyl and isotetracontyl or represented by formula (II)



50 where p may be 4, 5, 6, 7, 8, 9, 10 or 11;

or

R¹ is selected from the group consisting of isooctyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl, isotetra-decyl, isopentadecyl, isohexadecyl, isoheptadecyl, isoctadecyl, isononadecyl, isoeicosyl, isoheneicosyl, isodoco-syl, isotricosyl, isotetracosyl, isopentacosyl, isohexacosyl, isoheptacosyl, isoctacosyl, isononacosyl, isotriacontyl, isohentriacontyl, isodotriacontyl, isotritriacontyl, isotetratriacontyl, isopentatriacontyl, isohexatriacontyl, isoheptatri-acontyl, isoctatriacontyl, isononatriacontyl and isotetracontyl or represented by formula (II)



10 where p may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11,
 and R² is C₃₅-C₂₀₀ polyisobutene;

b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

15 c) ≥ 0.0 to ≤ 20 % by weight of at least one additive component,

whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11.

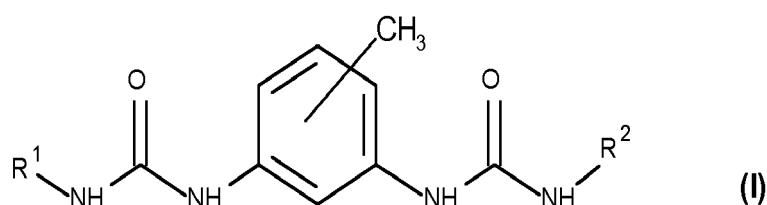
20 [0128] In a preferred embodiment, the presently claimed invention is directed to the use of composition in lubricant and grease formulations.

[0129] The lubricant compositions and uses according to the invention may in one embodiment be implemented in the context of a light, medium and heavy duty engine oil, industrial engine oil, marine engine oil, automotive engine oil, crankshaft oil, compressor oil, refrigerator oil, hydrocarbon compressor oil, very low-temperature lubricating oil and fat, 25 high temperature lubricating oil and fat, wire rope lubricant, textile machine oil, refrigerator oil, aviation and aerospace lubricant, aviation turbine oil, transmission oil, gas turbine oil, spindle oil, spin oil, traction fluid, transmission oil, plastic transmission oil, passenger car transmission oil, truck transmission oil, industrial transmission oil, industrial gear oil, insulating oil, instrument oil, brake fluid, transmission liquid, shock absorber oil, heat distribution medium oil, transformer oil, fat, chain oil, minimum quantity lubricant for metalworking operations, oil to the warm and cold working, oil for a 30 water-based metalworking liquid, oil for a neat oil working fluid, oil for a semi-synthetic metalworking fluid, oil for a synthetic metalworking fluid, drilling detergent for the soil exploration, hydraulic oil, biodegradable lubricant or lubricating grease or wax, chain saw oil, release agent, moulding fluid, gun, pistol and rifle lubricant or watch lubricant and food grade approved lubricant.

[0130] The preferred embodiments as described above also apply to the uses and methods as outlined in the following 35 passages.

[0131] In another aspect, the presently claimed invention is directed to the use of a composition comprising

a) ≥ 0.2 to ≤ 20 % by weight of at least one compound of general formula (I)



45 wherein

50 R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁₄-C₄₀-alkyl, or
 R¹ is linear or branched, substituted or unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

b) ≥ 80 to ≤ 99.50 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

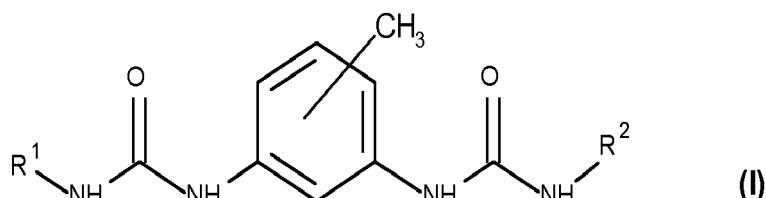
55 c) ≥ 0.0 to ≤ 20 % by weight of at least one additive component,

whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11

5 for reducing wear between rubbing surfaces of at least one first material and at least one second material, whereby the first and the second material are independently selected from the group consisting of metals, ceramics, fiber-reinforced composites, plastics and wood.

[0132] In a another aspect, the presently claimed invention is directed to the use of a composition in oil based lubricants or grease lubricants, comprising

10 a) ≥ 0.2 to $\leq 20\%$ by weight of at least one compound of general formula (I)



20 wherein

R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl,
or
R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

25 b) ≥ 80 to $\leq 99.50\%$ by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

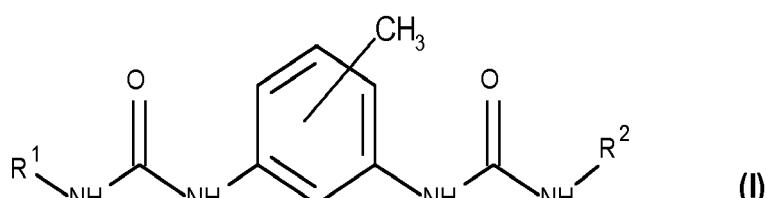
30 c) ≥ 0.0 to $\leq 20\%$ by weight of at least one additive component,

whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11 ;

35 for reducing wear between rubbing surfaces of at least one first material and at least one second material, whereby the first and the second material are independently selected from the group consisting of metals, ceramics, fiber-reinforced composites, plastics and wood.

[0133] In a another aspect, the presently claimed invention is directed to a method for reducing wear between rubbing surfaces of at least one first material and at least one second material, whereby the first and the second material are independently selected from the group consisting of metals, ceramics, fiber-reinforced composites, plastics and wood, comprising at least the step of applying a composition comprising

40 a) ≥ 0.2 to $\leq 20\%$ by weight of at least one compound of general formula (I)



50 wherein

R¹ and R², independently of one another, are branched, unsubstituted C₁₄-C₄₀-alkyl,
or
R¹ is branched, unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

55 b) ≥ 80 to $\leq 99.50\%$ by weight of at least one base oil selected from the group consisting of Group I mineral oils,

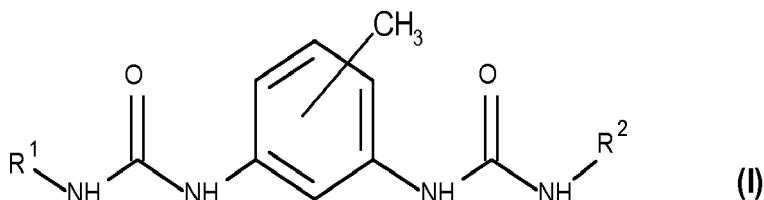
Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

c) ≥ 0.0 to ≤ 20 % by weight of at least one additive component,

5 whereby the sum of the weight percentages of the components a), b) and c) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 10 , onto the at least one first material.

10 [0134] In another aspect, the presently claimed invention is directed to a method for reducing wear between rubbing surfaces of at least one first material and at least one second material, whereby the first and the second material are independently selected from the group consisting of metals, ceramics, fiber-reinforced composites, plastics and wood, comprising at least the step of applying a composition comprising

15 a) ≥ 0.2 to ≤ 18 % by weight of at least one compound of general formula (I)



25 wherein

25 R^1 and R^2 , independently of one another, are branched, unsubstituted C_{14} - C_{40} -alkyl,

or

25 R^1 is branched, unsubstituted C_8 - C_{40} -alkyl and R^2 is C_{35} - C_{200} polyisobutene,

30 b) ≥ 80 to ≤ 95 % by weight of at least one base oil selected from the group consisting of Group I mineral oils, Group II mineral oils, Group III mineral oils, Group IV oils and Group V oils,

35 whereby the sum of the weight percentages of the components a) and b) adds up to 100 % by weight, characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11 , onto the at least one first material.

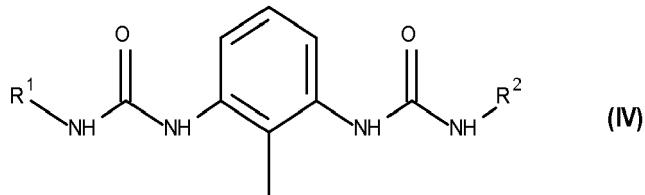
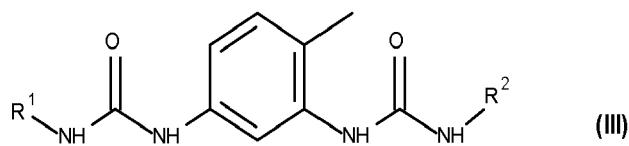
[0135] In the sense of the presently claimed invention, the term "rubbing" refers to solid surfaces in frictional contact with each other.

[0136] The materials that can be lubricated by the lubricating composition described herein and the inventively claimed method are not particularly limited and include materials such as ceramics, metals, composites, plastics, wood and combinations thereof. The rubbing surfaces involve two (or more) contacting surfaces of solid materials. The contacting surfaces are in relative motion to each other. For example, confronting surfaces of two separate solid bodies can both be moving in sliding contact over one another, or alternatively, one surface can be stationary while another surface of another body is set in motion to slide in contact over the surface of the stationary body. Also, the inventively claimed method can be used to lubricate a plurality of metal surfaces in rubbing contact, a plurality of ceramic surfaces in rubbing contact or both a metal surface and a ceramic surface in rubbing contact.

[0137] Metals that can be lubricated according to the presently claimed invention comprise steel, alloy steels, alloy cast iron, aluminum alloys, titanium alloys and other advanced high strength, high temperature metallic alloys. Ceramic materials that can be lubricated according to the presently claimed invention comprise alumina, zirconia, silicon nitride, silicon carbide, boron nitride, aluminum nitride, boron carbide and beryllia. Polymer matrix composites (e.g. carbon fiber/epoxy, glass fiber/nylon, carbon/polyether ether ketone and high temperature polymeric composites) also serve as materials to be lubricated according to the presently claimed invention.

[0138] In another embodiment, the presently claimed invention is directed to the use of at least one compound of general formula (I) as described herein for increasing the shear stability of a lubricant composition.

[0139] In another embodiment the presently claimed invention is directed to a compound of general formula (III) or (IV)



15 wherein R¹ is isotridecyl and R² is C₆₀-C₈₀ polyisobutene or

R¹ is isoheptadecyl and R² is C₆₀-C₈₀ polyisobutene or
R¹ is isoheptadecyl and R² is isoheptadecyl.

20 [0140] The lubricant composition of the present invention has excellent mechanical stability under shearing. The lubricant composition exhibit powerful thickening capacity in a wide range of base oils. The thickening property of the lubricant compositions of the present invention is effected even at lower concentration. The lubricant compositions exhibit viscoelastic properties at lower concentration as well as at higher concentration.

25 **Examples**

Compounds

[0141] Toluene 2,4-diisocyanate (TDI) 95%,

30 Oleylamine 70%,

1,5-Dimethylhexylamine 99%, are available from Aldrich.

[0142] 2-Ethylhexylamine (2-EHNH₂) 99%,

2-Propylheptylamine (2-PHNH₂),

Tridecylamine isomer mixture (iC₁₃H₂₇NH₂), CAS 86089-17-0,

35 Kerocom[®] PIBA (65% by weight solution of polyisobutylene amine based on high-reactivity polyisobutene, M_n=1000, in an aliphatic hydrocarbon mixture),

Irgaflo[®] 6100 V (alkyl methacrylate copolymer in a highly refined mineral oil),

Glissopal[®] 2300 (polyisobutylene with M_n = 2300 g/mol),

Cetiol[®] 868 (ethylhexyl stearate),

40 Synative[®] ES DPHA (di-(2-propyl-heptyl) adipate),

Irgalube[®] 8080 (Blend of high performance additives)

are available from BASF SE, Ludwigshafen, Germany.

45 [0143] Heptadecylamine isomer mixture (iC₁₇H₃₅NH₂) was obtained by alcohol amination of heptadecanol M (isomer mixture of primary heptadecanols, branched and linear, CAS 90388-00-4, from BASF SE) in a manner known in principle as described in EP 2547200 or EP 696572.

[0144] iC₁₄H₂₉NH₂ was obtained by alcohol amination of Isofol[®] 14T from Sasol as described in principle in EP 2547200 or EP 696572. Isofol[®] 14T is a mixture of different C₁₄ Guerbet alcohols. Isofol[®] 14T is a mixture of 10-20% 2-butyloctanol, 45-55% 2-butyldecanol or 2-hexyloctanol, and 25-35% 2-hexyldecanol.

50 [0145] iC₂₈H₅₇NH₂ was obtained by alcohol amination of Isofol[®] 28 from Sasol as described in principle in EP 2547200 or EP 696572. Isofol[®] 28 is a C₂₈ Guerbet alcohol and contains > 90% 2-dodecylhexadecanol.

[0146] Base oil Yubase[®] 4 was obtained from SK Lubricants. Yubase[®] 4 is a Grade III mineral oil with a kinematic viscosity of 4.24 mm²/s at 100°C, a viscosity index of 124, a Noack volatility of 14.5%, a Pour Point of -15°C, and sulfur content of 1.

55 **Methods**

[0147] The total amine number (titration with perchloric acid) was determined according to DIN EN ISO 9702.

[0148] The mean degree of branching was determined by ¹H NMR spectroscopy as follows: A sample of the alcohol

R¹/R²-OH, used for the preparation of the primary amine, was first derivatized with trichloroacetyl isocyanate (TAI) (J. Loccufier et al., Polymer Bulletin 27, 1991, 201). The signals of the esterified primary alcohols are situated at δ = 4.7 to 4.0 ppm, those of the esterified secondary alcohols (if present) at about 5 ppm, and water present in the sample reacts with TAI to give carbamic acid. All methyl, methylene and methine protons are situated in the range from 2.4 to 0.4 ppm.

5 The signals < 1 ppm here are assigned to the methyl groups. From the spectrum obtained in this way, the mean degree of branching (iso index) may be calculated as follows: Iso index = ((F(CH₃) / 3) / (F(CH₂-OH) / 2)) - 1 where F(CH₃) represents the signal area corresponding to the methyl protons, and F(CH₂-OH) represents the signal area of the methylene protons in the CH₂-OH group.

10 [0149] Number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity of polyisobutylene was determined by gel permeation chromatography (GPC): Eluent THF, column temperature 35°C, column material Pigel 10 μ m, length 30 cm, diameter 7.5 mm, guard column length 5 cm diameter 7.5 mm (Supplier Agilent). For calibration polyisobutylene standards (available from Polymer Standard Service) with M = 340 to M = 801000 have been used. Flow 1 mL/min, concentration 2 mg/mL, injection 100 μ L. Detector: DRI 1100 serie (Agilent).

15 **Preparation of diurea compounds of examples 1-8 and 10-15:**

20 [0150] A solution of the toluene 2,4-diisocyanate in dichloromethane (1.0 equivalent, 3.4 ml solvent/mmol diisocyanate) was admixed with a solution of the amine in dichloromethane (2.0 equivalents according to total amine number, 0.67 ml solvent/mmol amine) at room temperature. The exothermic reaction was cooled. After the addition was complete, stirring was continued at room temperature for 2 hours. The precipitated product was filtered and recrystallized from ethyl acetate.

Table 1

Example	Amine 1	Equivalents of amine 1	Amine 2	Equivalents of amine 2
1*	2-EHNH ₂	2.0	none	-
2*	2-PHNH ₂	2.0	none	-
3*	iC ₁₃ H ₂₇ NH ₂	2.0	none	-
4	iC ₁₇ H ₃₅ NH ₂	2.0	none	-
5*	Oleyl amine	2.0	none	-
6*	1,5-Dimethyl hexyl amine	2.0	none	-
7*	iC ₁₄ H ₂₉ NH ₂	2.0	none	-
8*	iC ₂₈ H ₅₇ NH ₂	2.0	none	-
10*	2-EHNH ₂	1.95	PIBA	0.05
11*	2-EHNH ₂	1.90	PIBA	0.10
12	2-EHNH ₂	1.80	PIBA	0.20
13	2-EHNH ₂	1.60	PIBA	0.40
14*	iC ₁₃ H ₂₇ NH ₂	1.95	PIBA	0.05
15	iC ₁₃ H ₂₇ NH ₂	1.90	PIBA	0.10
16	iC ₁₃ H ₂₇ NH ₂	1.80	PIBA	0.20
17	iC ₁₃ H ₂₇ NH ₂	1.60	PIBA	0.40
18	iC ₁₇ H ₃₅ NH ₂	1.80	PIBA	0.20

50 * = not within the scope of the invention

Preparation of diurea compounds of Example 9, according to S. Pensec, N. Nouvel, A. Guilleman, C. Creton, F. Boué', L. Bouteiller, Macromolecules 2010, 43, 2529.

55 [0151] Toluene 2,4-diisocyanate (1.0 equivalent) was added at room temperature and under nitrogen to a stirred solution of amino-functional polyisobutene (Kerocom® PIBA, 65% solution in hydrocarbon) (2.0 equivalents) in dry THF (20 ml per g toluene 2,4-diisocyanate). After stirring for 24 hours, the reaction mixture was precipitated under vigorous stirring in ethyl acetate (222 ml per g toluene 2,4-diisocyanate). A viscous oil decanted. After 24 hours, the upper phase

was eliminated, and the product was dried under vacuum for a month to give a rubbery solid product, 2,4-bis-(polyisobuteneureido)-toluene (molecular weight = 2260 g/mol).

Determination of the solubilities and rheology-modifying properties of the compounds 1-18 in Base oil, Yubase 4

5

[0152] For the determination of the solubilities, 0.5 g of the compound under test was stirred with 99.5 g of Yubase 4 at 100°C for 4 hours and subsequently cooled to room temperature. The appearance of the solution was assessed by visual inspection.

10

Table 2

Compound	Solubility 0.5% in Yubase 4; visible appearance	Average number of C atoms/alkyl chain	Mean degree of branching of alkyl chain
Example 1*	no clear solution	8	1
Example 2*	no clear solution	10	1
Example 3*	no clear solution	13	2.1
Example 4	clear solution, visibly more viscous than Yubase 4	17	3.1
Example 5*	no clear solution	18	0
Example 6*	no clear solution	8	2
Example 7*	no clear solution	14	1
Example 8*	clear solution, not visibly more viscous than Yubase 4	28	1
Example 9*	clear solution, not visibly more viscous than Yubase 4	71	35
Example 10*	no clear solution	9.6	1.9
Example 11*	no clear solution	11.2	2.7
Example 12	clear solution, visibly more viscous than Yubase 4	14.3	4.4
Example 13	clear solution, visibly more viscous than Yubase 4	20.6	7.8
Example 14*	no clear solution	14.5	2.9
Example 15	no clear solution	15.9	3.7
Example 16	clear solution, visibly more viscous than Yubase 4	18.8	5.4
Example 17	clear solution, visibly more viscous than Yubase 4	24.6	8.7
Example 18	clear solution, visibly more viscous than Yubase 4	22.4	6.3

* = not within the scope of the invention

55

[0153] The examples clearly demonstrate that only diurea compounds with a mean degree of branching of ≥ 3 lead to more viscous solutions that are still clear, i.e. do not form any particulate matter and/or form interfaces, and accordingly can be used as lubricants. If however, mean degree of branching is ≥ 11 , the viscosity of the solution does not increase.

[0154] Shear stability has been determined according to CEC L-45-A-99 (2014, Tapered Roller Bearing, test duration 20 hours) for compounds of example 4 and 16. Following results were obtained:

Table 3

Sample	KV 100 before test [mm ² /s]	KV 100 after test [mm ² /s]	Viscosity loss (rel.) [%]
0.5% compound of Example 16 in Yubase® 4	21.53	21.33	0.93
0.5% Compound of Example 4 in Yubase® 4	5.363	5.317	0.86

[0155] As comparative examples, the shear stabilities of the two known polymeric thickeners/viscosity index improvers Irgaflo® 6100 V and Glissopal® 2300 were determined. Following results were obtained:

Table 4

Sample	KV 100 before test [mm ² /s]	KV 100 after test [mm ² /s]	Viscosity loss (rel.) [%]
10% Irgaflo® 6100 V in Yubase® 4	9.003	6.272	30.30
15% Glissopal® 2300 in Yubase® 4	8.48	8.30	2.10

[0156] The inventive examples 4 and 16 showed a superior shear stability in comparison to the polymeric thickeners/viscosity index improvers. Example 16 demonstrates a higher thickening efficiency compared to the polymeric thickeners/viscosity index improvers.

Rheological measurements

[0157] Viscosities of different compounds (each 0.5% in Yubase 4 obtained from the solubility determinations. The relative viscosities (ratio of the viscosity of the solution to the viscosity of the solvent) of the solutions at 25°C were determined using a Stabinger viscometer (equivalent to ASTM D445).

[0158] The following results were obtained:

Table 5

Sample	Relative viscosity
Example 16 (inventive)	4.4
Example 4 (inventive)	4.8
Example 8 (non-inventive)	1.0
Example 9 (non-inventive)	1.0

[0159] The above Table 5 indicates that by adding inventive compounds having a mean degree of branching in the range of ≥ 3 to ≤ 11 , even in small quantities, a huge increase in the viscosity can be achieved.

Viscosity of compound of example 16 in different base oils:

[0160] The solubility and viscosifying effects of compound of example 16 was tested in different base oils. In each case, clear 0.5% solutions were obtained by heating the diurea in the respective solvent at 100°C until complete dissolution. The relative viscosities (ratio of the viscosity of the solution to the viscosity of the solvent) of the solutions at 25°C were determined using a Stabinger viscometer (equivalent to ASTM D445).

[0161] The following results were obtained:

Table 6

Solvent	Base Oil Class	Relative viscosity
Yubase® 4	Group III	4.4
Cetiol® 868 (BASF SE)	Group V	4.6
Synative® ES DPHA (BASF SE)	Group V	3.8
PAO 2	Group IV	5.1
PAO 4	Group IV	3.3

[0162] The above table indicates that the inventive compounds are compatible with a wide range of base oils.

Viscoelasticity determination:

[0163]

Solution A: 20% compound of example 13 in Yubase 4

Solution B: 10% compound of example 4 in Yubase 4

Solution C: 0.5% compound of example 16 in Yubase 4

[0164] Complex viscosity of compounds of example 13, 4 and 16 was measured in Yubase 4. Solution A, B, C were prepared by heating compounds of example 13, 4 and 16 respectively in Yubase 4 at 100°C until complete dissolution.

[0165] The rheological data of complex viscosities, storage modulus and loss modulus were determined on an ARES G2 rheometer from TA Instruments. The geometry used was a concentric cylinder device of Couette type with rotating cup. The diameters of cup and bob are 20 mm and 18.6 mm, respectively. The bob is of DIN type (with conical end) and has a length of 27.9 mm. The measurement profile was a temperature ramp with 2°C/min at constant angular frequency of 10 rad/s and a constant strain amplitude of 20%.

[0166] The following results were obtained:

Table 7

Solution	T [°C]	Storage modulus [Pa]	Loss modulus [Pa]	Complex viscosity [Pa.s]
A	25	20,7309	11,0509	2,3492
A	30	18,9508	9,8682	2,1366
A	40	15,1981	8,3737	1,7352
A	50	11,2436	7,4049	1,3463
A	60	7,0022	6,4004	0,9487
A	70	2,7122	4,4990	0,5253
A	80	0,2987	1,5436	0,1572
A	90	0,0159	0,2094	0,0210
A	100	0,0005	0,0410	0,0040
Solution	T [°C]	Storage modulus [Pa]	Loss modulus [Pa]	Complex viscosity [Pa.s]
B	25	15,4515	8,8773	1,7820
B	30	14,3169	8,1218	1,6460
B	40	11,4836	7,0574	1,3479
B	50	8,6578	6,2099	1,0655
B	60	6,1283	5,4321	0,8189
B	70	3,5286	4,4238	0,5658

(continued)

Solution	T [°C]	Storage modulus [Pa]	Loss modulus [Pa]	Complex viscosity [Pa.s]
B	80	1,0180	2,6137	0,2805
	90	0,0213	0,1358	0,0138
	100	0,0007	0,0482	0,0048
C	25	12,5158	5,0757	1,3506
	30	11,2576	4,2578	1,2036
	40	10,4059	3,3350	1,0927
C	50	9,5468	2,7607	0,9938
	60	8,6332	2,4783	0,8982
	70	7,3629	2,4387	0,7756
C	80	5,4659	2,6805	0,6088
	90	2,1444	2,5801	0,3355
	100	0,0888	0,5897	0,0596

[0167] These results show that all the three solutions have viscoelastic properties. Thus, the compounds of the present invention exhibit viscoelasticity at lower concentration of 0.5% as well as at a higher concentration of 20%.

Example 19: Preparation of a grease composition

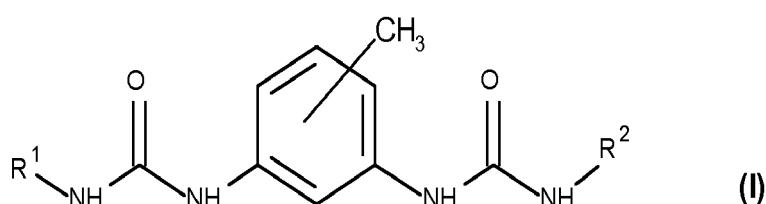
[0168] Compound 16 (75 g) was dissolved in Yubase® 4 (425 g) with stirring at 100°C. Unworked penetration (according to ISO 2137:1985-11) was determined to be 325 units.

Example 20: Preparation of a hydraulic fluid

[0169] Compound 16 (0.7 g) and Irgalube® 8080 (0.4 g) were dissolved at 90°C in Cetiol® 868 (98.9 g) with stirring until complete dissolution. Kinematic viscosity of the solution at 40°C (Stabinger viscometer, equivalent to ASTM D445): 44 mm²/s.

Claims

1. Use of at least one compound of general formula (I) as thickening agent



wherein

R¹ and R², independently of one another, are linear or branched, substituted or unsubstituted C₁₄-C₄₀-alkyl, or

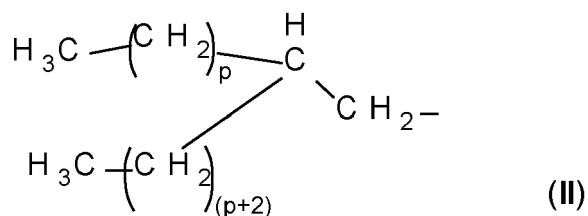
R¹ is linear or branched, substituted or unsubstituted C₈-C₄₀-alkyl and R² is C₃₅-C₂₀₀ polyisobutene,

characterized in that the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 11 .

2. The use according to claim 1, whereby the at least one compound of general formula (I) has a mean degree of branching (iso-index) in the range of ≥ 3 to ≤ 9 .

5 3. The use according to claim 1, whereby R¹ and R² are, independently of one another, selected from the group consisting of n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-eicosyl, n-heneicosyl, n-docosyl, n-tricosyl, n-tetracosyl, n-pentacosyl, n-hexacosyl, n-heptacosyl, n-octacosyl, n-nonacosyl, n-triacontyl, n-hentriacontyl, n-dotriacontyl, n-tritriacontyl, n-tetratriacontyl, n-pentatriacontyl, n-hexatriacontyl, n-heptatriacontyl, n-octatriacontyl, n-nonatriacontyl, n-tetracontyl, isotetradecyl, isopentadecyl, isohexadecyl, isohexadecyl, isooctadecyl, isononadecyl, isoeicosyl, isoheneicosyl, isodocosyl, isotricosyl, isotetracosyl, isopentacosyl, isohexacosyl, isoheptacosyl, isooctacosyl, isononacosyl, isotriacontyl, isohentriacontyl, isodotriacontyl, isotritriacontyl, isotetratriacontyl, isopentatriacontyl, isohexatriacontyl, isoheptatriacontyl, isooctatriacontyl, isononatriacontyl and isotetracontyl or represented by formula (II)

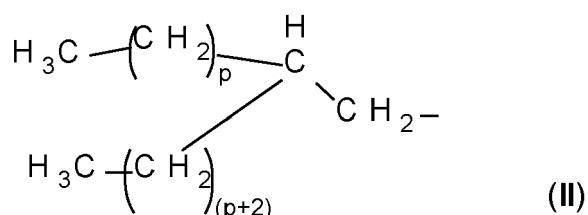
10



where p may be 4, 5, 6, 7, 8, 9, 10 or 11.

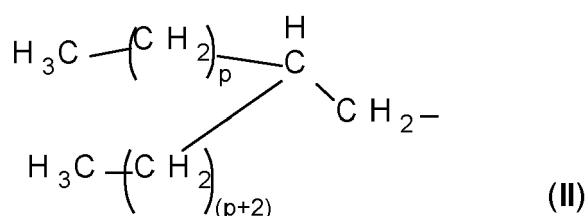
25 4. The use according to claim 1, whereby R¹ is selected from the group consisting of n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-eicosyl, n-heneicosyl, n-docosyl, n-tricosyl, n-tetracosyl, n-pentacosyl, n-hexacosyl, n-heptacosyl, n-octacosyl, n-nonacosyl, n-triacontyl, n-hentriacontyl, n-dotriacontyl, n-tritriacontyl, n-tetratriacontyl, n-pentatriacontyl, n-hexatriacontyl, n-heptatriacontyl, n-octatriacontyl, n-nonatriacontyl, n-tetracontyl, iso-octyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl, isotetradecyl, isopentadecyl, isohexadecyl, isohexadecyl, isooctadecyl, isononadecyl, isoeicosyl, isoheneicosyl, isodocosyl, isotricosyl, isotetracosyl, isopentacosyl, isohexacosyl, isoheptacosyl, isooctacosyl, isononacosyl, isotriacontyl, isohentriacontyl, isodotriacontyl, isotritriacontyl, isotetratriacontyl, isopentatriacontyl, isohexatriacontyl, isoheptatriacontyl, isooctatriacontyl, isononatriacontyl and isotetracontyl or represented by formula (II)

30



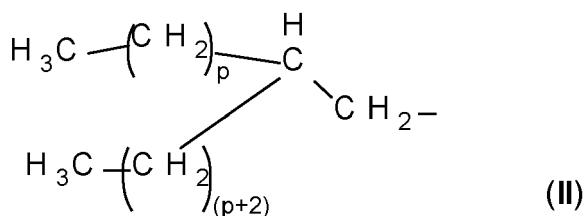
where p may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11,
and R² is C₃₅-C₂₀₀ polyisobutene.

45 5. The use according to claim 3, whereby R¹ and R² are, independently of one another, selected from the group consisting of isotetradecyl, isopentadecyl, isohexadecyl, isoheptadecyl, isooctadecyl, isononadecyl and isoeicosyl or represented by formula (II)



where p may be 4, 5, 6 or 7.

6. The use according to claim 4, whereby R^1 is selected from the group consisting of isoocetyl, isononyl, isodecyl, isoundecyl, isododecyl, isotridecyl, isotetradecyl, isopentadecyl, isohexadecyl, isoheptadecyl, isoocadecyl, isononadecyl and isoeicosyl or represented by formula (II)



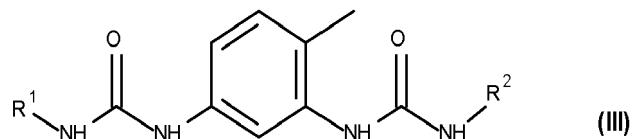
wear agents, detergents, corrosion inhibitors, extreme pressure agents, metal deactivators, rust inhibitors and pour point depressants.

14. Use of compositions according to claim 8 in lubricant or grease formulations.

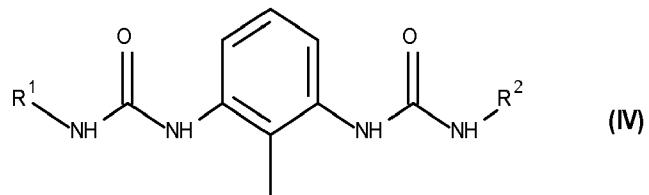
5

15. A compound of general formula (III) or (IV)

10



15



20

whereby R¹ is isotridecyl and R² is C₆₀-C₈₀ polyisobutene or R¹ is isoheptadecyl and R² is C₆₀-C₈₀ polyisobutene or R¹ is isoheptadecyl and R² is isoheptadecyl.

25

30

35

40

45

50

55



EUROPEAN SEARCH REPORT

Application Number

EP 16 18 8542

5

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
10 X,D	US 4 668 411 A (YASUI HIROYOSHI [JP] ET AL) 26 May 1987 (1987-05-26) * column 1, line 52 - line 66; claims 1-6 * * column 3, line 9 *	15 1-14	INV. C10M115/08
15 A	----- US 4 780 231 A (KINOSHITA HIROTUGU [JP] ET AL) 25 October 1988 (1988-10-25) * claim 1 *	1-15	
20 A,D	----- US 2004/242439 A1 (MIKAMI HIDENOBU [JP] ET AL) 2 December 2004 (2004-12-02) * paragraph [0035] - paragraph [0037] *	1-15	
25			
30			TECHNICAL FIELDS SEARCHED (IPC)
35			C10M C10N
40			
45			
50 1	The present search report has been drawn up for all claims		
55	Place of search Munich	Date of completion of the search 15 November 2016	Examiner 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			

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

EP 16 18 8542

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

15-11-2016

10	Patent document cited in search report	Publication date		Patent family member(s)	Publication date
15	US 4668411 A	26-05-1987	JP	H0524958 B2	09-04-1993
			JP	S61155496 A	15-07-1986
			US	4668411 A	26-05-1987
20	US 4780231 A	25-10-1988	JP	H0660316 B2	10-08-1994
			JP	S62250097 A	30-10-1987
			US	4780231 A	25-10-1988
25	US 2004242439 A1	02-12-2004	JP	4334915 B2	30-09-2009
			JP	2004352858 A	16-12-2004
			US	2004242439 A1	02-12-2004
30					
35					
40					
45					
50					
55					

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- EP 2467461 A [0007]
- EP 1602710 A [0008]
- EP 2716745 A [0009]
- US 20140254968 A [0010]
- US 8044005 B [0011]
- US 7786058 B [0012]
- US 5059336 A [0013]
- US 4668411 A [0014]
- WO 2004087808 A [0045]
- US 5362378 A [0054]
- US 5565086 A [0054]
- US 5246566 A [0054]
- US 5135638 A [0054]
- EP 710710 A [0054]
- EP 321302 A [0054]
- EP 321304 A [0054]
- US 3149178 A [0057]
- US 3382291 A [0057]
- US 3742082 A, Brennan [0057]
- US 3769363 A, Brennan [0057]
- US 3876720 A, Heilman [0057]
- US 4239930 A, Allphin [0057]
- US 4367352 A, Watts [0057]
- US 4413156 A, Watts [0057]
- US 4434308 A, Larkin [0057]
- US 4910355 A, Shubkin [0057]
- US 4956122 A, Watts [0057]
- US 5068487 A, Theriot [0057]
- WO 2008014315 A [0082]
- US 3087936 A [0091]
- US 3254025 A [0091]
- US 4234435 A [0110]
- US 3172892 A [0110]
- US 3381022 A [0110]
- EP 2547200 A [0143] [0144] [0145]
- EP 696572 A [0143] [0144] [0145]

Non-patent literature cited in the description

- Alcohols, Aliphatic. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, 2008, 10 [0039]
- **F. LORTIE.** *Langmuir*, 2002, vol. 18, 7218 [0048]
- Engine Oil Licensing and Certification System. Industry Services Department, 1996 [0054]
- **KIRK ; OTHMER.** Encyclopedia of Chemical Technology [0097]
- Fats and Fatty Oils. vol. 9, 795-831 [0097]
- Lecithins. vol. 14, 250-269 [0097]
- **J. LOCCUFIER et al.** *Polymer Bulletin*, 1991, vol. 27, 201 [0148]