



(11)

EP 2 752 480 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

09.07.2014 Bulletin 2014/28

(21) Application number: **12828806.5**

(22) Date of filing: **30.08.2012**

(51) Int Cl.:

C10M 169/04 (2006.01)	C10M 105/38 (2006.01)
C10M 105/42 (2006.01)	C10M 137/08 (2006.01)
C10N 20/00 (2006.01)	C10N 20/02 (2006.01)
C10N 30/00 (2006.01)	C10N 30/02 (2006.01)
C10N 30/06 (2006.01)	C10N 30/10 (2006.01)
C10N 40/02 (2006.01)	C10N 40/04 (2006.01)

(86) International application number:

PCT/JP2012/072011

(87) International publication number:

WO 2013/031894 (07.03.2013 Gazette 2013/10)

(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**

(30) Priority: **02.09.2011 JP 2011192083**

(71) Applicant: **Idemitsu Kosan Co., Ltd**
Tokyo 100-8321 (JP)

(72) Inventors:

- **OHNO Takuya**
Ichihara-shi
Chiba 299-0107 (JP)
- **GOTO Masahisa**
Ichihara-shi
Chiba 299-0107 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) **BIODEGRADABLE LUBRICATING OIL COMPOSITION**

(57) A biodegradable lubricating oil composition of the invention includes a component (A) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid and a linear aliphatic dicarboxylic acid with a polyhydric alcohol, a component (B) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid with a polyhydric alcohol, and a component (C) that is a phosphate amine salt obtained by reacting an acidic

phosphate with an alkylamine, in which the linear saturated aliphatic carboxylic acid of the component (A) is formed of a linear saturated aliphatic carboxylic acid having 8 carbon atoms and a linear saturated aliphatic carboxylic acid having 10 carbon atoms, and a molar amount of the linear saturated aliphatic carboxylic acid having 8 carbon atoms is larger than a molar amount of the linear saturated aliphatic carboxylic acid having 10 carbon atoms.

EP 2 752 480 A1

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a lubricating oil composition. More specifically, the present invention relates to a biodegradable lubricating oil composition to be used for a step-up gear used, in particular, for wind power generation.

BACKGROUND ART

10 **[0002]** In recent years, in view of environmental issues and exhaustion of fossil fuels, wind power generation, which uses natural energy, has been receiving considerable attention. Since it is important to increase power generation efficiency due to a low rotation speed of a rotor in wind power generation, a step-up gear is provided in a power generator. A so-called gear oil is used to lubricate a gear mechanism used in the step-up gear, and is required to provide a considerably high lubricity.

15 **[0003]** Typically, a lubricating oil whose base oil is PAO (polyalphaolefin) has been used as a step-up gear oil. Since a wind power generator is often used on the ocean or under the natural environment, the step-up gear oil needs to be highly biodegradable. The typical PAO lubricating oil, however, has little biodegradability, so that an alternative thereto has been sought.

20 **[0004]** Since a lubricating oil for a step-up gear in a wind power generator needs to be biodegradable, application of a lubricating oil including an ester as a base oil is conceivable (see, for instance, Patent Literatures 1 to 3). Each of Patent Literatures 1 and 2 has proposed a biodegradable lubricating oil whose base oil is a complex ester obtained from a polyhydric alcohol and a polycarboxylic acid. Patent Literature 2 has proposed a biodegradable lubricating oil provided by blending two specific kinds of complex esters and a specific phosphate amine salt.

25 CITATION LIST

PATENT LITERATURES

[0005]

30 Patent Literature 1 JP-A-2003-522204

Patent Literature 2 JP-A-2005-520038

35 Patent Literature 3 JP-A-2010-260972

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

40 **[0006]** The biodegradable lubricating oils disclosed in Patent Literatures 1 and 2 do not have a sufficient oxidation stability, so that, when being used for a step-up gear in a wind power generator, the biodegradable lubricating oils are unlikely to continuously exhibit properties as a lubricating oil for a long time.

45 **[0007]** Moreover, since the biodegradable lubricating oil disclosed in Patent Literature 3 exhibits an insufficient low-temperature fluidity, when being used for a step-up gear in a wind power generator, for instance, in cold regions, the biodegradable lubricating oil causes a large increase in torque for operating devices, thereby decreasing power generation efficiency of a wind power generator and the like.

50 **[0008]** Accordingly, an object of the invention is to provide a biodegradable lubricating oil composition that is excellent in lubricity, low-temperature fluidity, oxidation stability and biodegradability and is also suitable for a step-up gear used in a wind power generator.

MEANS FOR SOLVING THE PROBLEMS

55 **[0009]** In order to solve the above problem, the following biodegradable lubricating oil composition is provided according to an aspect of the invention.

[0010] According to an aspect of the invention, a biodegradable lubricating oil composition includes: a component (A) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid and a linear aliphatic dicarboxylic acid with a polyhydric alcohol, the ester having a kinematic viscosity at 40 degrees C in a range from 400 mm²/s to 1000

mm²/s and an acid value of 0.5 mgKOH/g or less; a component (B) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid with a polyhydric alcohol, the ester having an acid value of 0.5 mgKOH/g or less; and a component (C) that is a phosphate amine salt obtained by reacting an acidic phosphate with an alkylamine, in which the linear saturated aliphatic carboxylic acid in the component (A) is formed of a linear saturated aliphatic carboxylic acid having 8 carbon atoms and a linear saturated aliphatic carboxylic acid having 10 carbon atoms, and a molar amount of the linear saturated aliphatic carboxylic acid having 8 carbon atoms is larger than a molar amount of the linear saturated aliphatic carboxylic acid having 10 carbon atoms.

[0011] In the biodegradable lubricating oil composition according to the above aspect of the invention, the linear saturated aliphatic carboxylic acid in the component (A) is preferably formed of the linear saturated aliphatic carboxylic acid having 8 carbon atoms in a range from 60 mol% to 90 mol% and the linear saturated aliphatic carboxylic acid having 10 carbon atoms in a range from 10 mol% to 40 mol%.

[0012] In the biodegradable lubricating oil composition according to the above aspect of the invention, the biodegradable lubricating oil is preferably a gear oil or a bearing oil. Moreover, the gear oil is preferably used for a step-up gear of a wind power generator.

[0013] The biodegradable lubricating oil composition according to the above aspect of the invention is excellent in lubricity, low-temperature fluidity, oxidation stability and biodegradability, and thus is also suitable for a step-up gear used in a wind power generator.

DESCRIPTION OF EMBODIMENT(S)

[0014] A biodegradable lubricating oil composition according to an exemplary embodiment of the invention (hereinafter also referred to simply as "the composition") is provided by blending a component (A) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid and a linear aliphatic dicarboxylic acid with a polyhydric alcohol, a component (B) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid with a polyhydric alcohol, and a component (C) that is a phosphate amine salt obtained by reacting an acidic phosphate with an alkylamine, in which the linear saturated aliphatic carboxylic acid of the component (A) is formed of a linear saturated aliphatic carboxylic acid having 8 carbon atoms and a linear saturated aliphatic carboxylic acid having 10 carbon atoms, and a molar amount of the linear saturated aliphatic carboxylic acid having 8 carbon atoms is larger than a molar amount of the linear saturated aliphatic carboxylic acid having 10 carbon atoms. A detailed description of this exemplary embodiment will be made below.

Component (A)

[0015] The component (A) of the exemplary embodiment is a so-called complex ester obtained by reacting a linear saturated aliphatic carboxylic acid and a linear aliphatic dicarboxylic acid with a polyhydric alcohol.

[0016] The linear saturated aliphatic carboxylic acid, which is formed of a linear saturated aliphatic carboxylic acid having 8 carbon atoms and a linear saturated aliphatic carboxylic acid having 10 carbon atoms, is a monovalent carboxylic acid. Moreover, it is required that the molar amount of the linear saturated aliphatic carboxylic acid having 8 carbon atoms is larger than the molar amount of the linear saturated aliphatic carboxylic acid having 10 carbon atoms. When the molar amount of the linear saturated aliphatic carboxylic acid having 8 carbon atoms is equivalent to or less than the molar amount of the linear saturated aliphatic carboxylic acid having 10 carbon atoms, the obtained biodegradable lubricating oil composition exhibits an insufficient oxidation stability.

[0017] A content of the linear saturated aliphatic carboxylic acid having 8 carbon atoms in a total amount of the linear saturated aliphatic carboxylic acid is preferably in a range of 51 mol% to 99 mol% at a molar ratio, more preferably in a range of 60 mol% to 90 mol%. When the content of the linear saturated aliphatic carboxylic acid having 8 carbon atoms falls within the above range, a secure oxidation stability of the obtained biodegradable lubricating oil composition can be ensured.

[0018] The linear saturated aliphatic carboxylic acid having 8 carbon atoms and the linear saturated aliphatic carboxylic acid having 10 carbon atoms are respectively exemplified by caprylic acid (8 carbon atoms) and capric acid (10 carbon atoms).

[0019] Examples of the linear aliphatic dicarboxylic acid include adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid, tetradecanedioic acid, pentadecanedioic acid, octadecanedioic acid, nonadecanedioic acid and eicosanedioic acid. For esterification, one of the above examples of the linear aliphatic dicarboxylic acid may be used alone or, alternatively, two or more thereof may be used in combination.

[0020] Among the above examples of the linear aliphatic dicarboxylic acid, one having 12 carbon atoms or less is preferably used to maintain fluidity at a low temperature.

[0021] As the polyhydric alcohol used to provide the component (A), a so-called hindered polyol is preferably used. Examples of the hindered polyol include neopentyl glycol, 2-ethyl-2-methyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, trimethylol ethane, trimethylol propane, trimethylol butane, trimethylol pentane, trimethylol hexane, trimethylol heptane,

pentaerythritol, 2,2,6,6-tetramethyl-4-oxa-1,7-heptanediol, 2,2,6,6,10,10-hexamethyl-4,8-dioxa-1,11-undecanediol, 2,2,6,6,10,10,14,14-octamethyl-4,8,12-trioxa-1,15-pentadecanediol, 2,6-dihydroxymethyl-2,6-dimethyl-4-oxa-1,7-heptanediol, 2,6,10-trihydroxymethyl-2,6,10-trimethyl-4,8-dioxa-1,11-undecanediol, 2,6,10,14-tetrahydroxymethyl-2,6,10,14-tetramethyl-4,8,12-trioxa-1,15-pentadecanediol, di(pentaerythritol), tri(pentaerythritol), tetra(pentaerythritol), and penta(pentaerythritol).

[0022] For esterification, one of the above examples of the hindered polyol may be used alone or, alternatively, two or more thereof may be used in combination.

[0023] The complex ester as the component (A) is obtained by reacting the above linear saturated aliphatic carboxylic acid and linear aliphatic dicarboxylic acid with polyhydric alcohol, and has a kinematic viscosity at 40 degrees C in a range from 400 mm²/s to 1000 mm²/s. When the kinematic viscosity is less than 400 mm²/s, the resulting lubricating oil composition is unlikely to have a viscosity required for maintaining lubricity. When the kinematic viscosity is more than 1000 mm²/s, the biodegradability of the resulting lubricating oil composition is likely to be lowered.

[0024] The component (A) is required to have an acid value of 0.5 mgKOH/g or less. When the acid value is more than 0.5 mgKOH/g, oxidation stability of the resulting lubricating oil composition is likely to be deteriorated.

[0025] In order to obtain an ester as the component (A), two kinds of carboxylic acids and a polyhydric alcohol are generally reacted with each other as described above. However, the ester may be obtained in a different way as long as the resulting ester structure includes the above carboxylic acid residue and polyhydric alcohol residue. Starting materials (reactants) are not necessarily the above carboxylic acids and polyhydric alcohol, and, furthermore, the component (A) does not necessarily have to be composited based on dehydration reaction thereof. The component (A) may be composited from other materials in a different way. For instance, the component (A) may be produced by transesterification.

Component (B)

[0026] The component (B) of the exemplary embodiment is an ester obtained by reacting a linear saturated aliphatic carboxylic acid with a polyhydric alcohol.

[0027] For maintaining biodegradability and low-temperature fluidity, a carboxylic acid having 6 to 12 carbon atoms is preferably used as the linear saturated aliphatic carboxylic acid. Examples of such a carboxylic acid include monocarboxylic acids such as caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecane acid and lauric acid. Since using one kind of carboxylic acid alone may result in solidification, several kinds of carboxylic acids are preferably combined in use.

[0028] As the polyhydric alcohol, a hindered polyalcohol is preferably used in the same manner as the polyhydric alcohol used to provide the component (A).

[0029] The component (B) preferably has a kinematic viscosity at 40 degrees C in a range from 20 mm²/s to 40 mm²/s. When the kinematic viscosity is less than 20 mm²/s, the lubricity of the resulting lubricating oil composition is likely to be lowered. On the other hand, when the kinematic viscosity is more than 40 mm²/s, the low-temperature fluidity of the resulting lubricating oil composition is likely to be deteriorated.

[0030] The component (B) is required to have an acid value of 0.5 mgKOH/g or less. When the acid value is more than 0.5 mgKOH/g, oxidation stability of the resulting lubricating oil composition is likely to be deteriorated.

[0031] An ester as the component (B) is generally obtained by reacting the above predetermined carboxylic acid and polyhydric alcohol with each other. However, the ester may be obtained in a different way as long as the resulting ester structure includes the above carboxylic acid residue and polyhydric alcohol residue. Starting materials (reactants) are not necessarily the above carboxylic acids and polyhydric alcohol, and, furthermore, the component (B) does not necessarily have to be composited based on dehydration reaction thereof. The component (B) may be composited from other materials in a different way. For instance, the component (B) may be produced by transesterification.

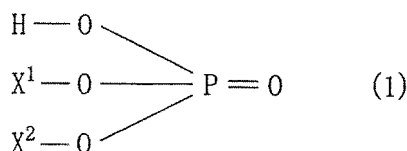
[0032] The blend ratio of the component (B) of the exemplary embodiment is preferably 10 mass% or more of the total amount of the composition in terms of biodegradability.

Component (C)

[0033] The component (C) of the exemplary embodiment is a phosphate amine salt obtained by reacting an acidic phosphate with an alkylamine.

[0034] The acidic phosphate used to provide the component (C) is exemplified by one having the structure represented by the following formula (1).

[Formula 1]



[0035] In the formula (1), X¹ is a hydrogen atom or an alkyl group having 6 to 20 carbon atoms, and X² is an alkyl group having 6 to 20 carbon atoms. The above alkyl group having 6 to 20 carbon atoms may have a linear, branched, or cyclic structure. Examples of the alkyl group include various hexyl groups, octyl groups, decyl groups, dodecyl groups, tetradecyl groups, hexadecyl groups, octadecyl groups and icosyl groups. Among the above, an alkyl group having 8 to 18 carbon atoms is preferable and an alkyl group having 8 to 13 carbon atoms is more preferable.

[0036] Examples of acidic alkyl phosphates represented by the formula (1) include acidic monophosphates such as monooctyl acid phosphate, monodecyl acid phosphate, monoisodecyl acid phosphate, monolauryl acid phosphate, mono(tridecyl) acid phosphate, monomyristyl acid phosphate, monopalmityl acid phosphate and monostearyl acid phosphate; and acidic diphosphates such as dioctyl acid phosphate, didecyl acid phosphate, diisodecyl acid phosphate, dilauryl acid phosphate, di(tridecyl) acid phosphate, dipalmityl acid phosphate and distearyl acid phosphate.

[0037] The component (C) may be provided using one of the above examples of the acidic phosphate alone or a combination of two or more thereof. Incidentally, the content of phosphorus (P) is preferably in a range from 150 mass ppm to 500 mass ppm of the total amount of the resulting composition. If the content of P is less than 150 mass ppm, the composition is likely to exhibit an insufficient seizure resistance when used as a gear oil. On the other hand, if the content of P is more than 500 mass ppm, the fatigue resistance (FZG micropitting resistance) of the composition is likely to be lowered. The content of P is preferably in a range from 250 mass ppm to 450 mass ppm, more preferably in a range from 350 mass ppm to 400 mass ppm.

[0038] The alkylamine used to provide the component (C) may be any one of primary amine, secondary amine and tertiary amine, but is preferably secondary amine and tertiary amine in terms of improvement of seizure resistance, more preferably dialkylamine or trialkylamine. Moreover, the phosphate amine salt in a liquid phase at room temperature (25 degrees C) is preferable in terms of solubility and prevention of precipitation at a low temperature in a base oil. In view of this, the alkylamine is preferably one having 6 to 20 carbon atoms.

[0039] Examples of dialkylamines include dihexylamine, dicyclohexylamine, dioctylamine, dilaurylamine and distearylamine. Examples of trialkylamines include trihexylamine, tricyclohexylamine, trioctylamine, trilaurylamine and tristearylamine.

[0040] One of the above examples of the alkylamine may be used alone or, alternatively, two or more thereof may be used in combination. In terms of seizure resistance, the alkylamine is favorably selected from the trialkylamines.

[0041] A content of the component (C) is preferably in a range from 0.2 mass% to 1 mass% of the total amount of the composition. The content less than 0.2 mass% provides a poor effect on reducing friction. On the other hand, the content more than 1 mass% is likely to decrease the fatigue resistance (FZG micropitting resistance). Herein, the component (C) in a resulting form of the acidic phosphate amine salt may be blended with other components to prepare the composition. Alternatively, the acidic phosphate and the alkylamine may be independently blended with other components to prepare the composition.

[0042] It should be noted that, in the instance where the acidic phosphate and the alkylamine are independently blended to prepare the composition, the total amount of the acidic phosphate and the alkylamine equals the content of the component (C).

[0043] The composition may further be added with a predetermined sulfur compound as a component (D) to enhance the lubricity. The component (D) is preferably exemplified by a sulfur compound (D-1) that does not contain a polysulfide condensation of -S-S-S- or more in a molecule and that contains 15 mass% or more of sulfur atoms (S) in the molecule. Further, the component (D-1) is additionally blended with a sulfur compound (D-2), which is preferably a trihydrocarbyl thiophosphate represented by the following formula (2).



[0044] In the formula (2), R is a hydrocarbyl group having 6 to 20 carbon atoms. When the sulfur compound as the component (D-1) is a compound having a polysulfide condensation of -S-S-S- or more in the molecule, generation of sludge is likely to be increased in an oxidation stability test (described below) and, furthermore, the FZG micropitting resistance is likely to be lowered. When the content of S in the molecule is less than 15 mass%, the effect provided by adding the sulfur compound may occasionally be insufficient, resulting in a shortage of the seizure resistance.

[0045] The sulfur compound as the component (D-1) having the above properties is exemplified by the following compounds:

- (1) a mono- or di-olefin sulfide;
 (2) a dihydrocarbyl mono- or di-sulfide;
 (3) a thiadiazole compound;
 (4) a dithiocarbamate compound;
 (5) an ester compound having a disulfide structure; and
 (6) other sulfur compounds.

Mono- or Di-olefin Sulfide

[0046] The olefin sulfide can be exemplified by a compound represented by the following formula (3).



[0047] In the formula (3), R^1 represents an alkenyl group having 2 to 15 carbon atoms, R^2 represents an alkyl or alkenyl group having 2 to 15 carbon atoms, and a represents an integer of 1 or 2. The compound is obtained by reacting an olefin having 2 to 15 carbon atoms or any one of the dimer to tetramer thereof with a sulfurizing agent such as sulfur, sulfur chloride or the like. Preferred examples of the olefin include propylene, isobutene and diisobutene.

Dihydrocarbyl Mono- or Di-sulfide

[0048] The dihydrocarbyl mono- or di-sulfide can be exemplified by a compound represented by the following formula (4).



[0049] In the formula (4), each of R^3 and R^4 represents an alkyl group having 1 to 20 carbon atoms, a cyclic alkyl group, an aryl group having 6 to 20 carbon atoms, an alkylaryl group having 7 to 20 carbon atoms or an arylalkyl group having 7 to 20 carbon atoms. R^3 and R^4 may be mutually the same or different. b represents an integer of 1 or 2. When R^3 and R^4 are both alkyl groups, the compound is referred to as an alkyl sulfide.

[0050] Preferred examples of the dihydrocarbyl mono- or di-sulfide represented by the above formula (4) include dibenzil mono- or di-sulfides, various dinonyl mono- or di-sulfides, various didodecyl mono- or di-sulfides, various dibutyl mono- or di-sulfides, various dioctyl mono- or di-sulfides, diphenyl mono- or di-sulfides, and dicyclohexyl mono- or di-sulfides.

Thiadiazole Compound

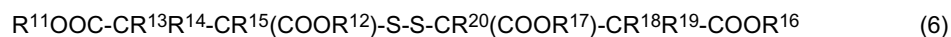
[0051] Preferred examples of the thiadiazole compound include 2,5-bis(n-hexyldithio)-1,3,4-thiadiazole, 2,5-bis(n-octyldithio)-1,3,4-thiadiazole, 2,5-bis(n-nonyldithio)-1,3,4-thiadiazole, 2,5-bis(1,1,3,3-tetramethylbutyldithio)-1,3,4-thiadiazole, 3,5-bis(n-hexyldithio)-1,2,4-thiadiazole, 3,6-bis(n-octyldithio)-1,2,4-thiadiazole, 3,5-bis(n-nonyldithio)-1,2,4-thiadiazole, 3,5-bis(1,1,3,3-tetramethylbutyldithio)-1,2,4-thiadiazole, 4,5-bis(n-octyldithio)-1,2,3-thiadiazole, 4,5-bis(n-nonyldithio)-1,2,3-thiadiazole, and 4,5-bis(1,1,3,3-tetramethylbutyldithio)-1,2,3-thiadiazole.

Dithiocarbamate Compound

[0052] The dithiocarbamate compound is exemplified by alkylene bisdialkyl dithiocarbamates, among which a preferable compound has an alkylene group having 1 to 3 carbon atoms, a linear or branched saturated or unsaturated alkyl group having 3 to 20 carbon atoms, or a cyclic alkyl group having 6 to 20 carbon atoms. Examples of the dithiocarbamate compound include methylene bisdibutyldithiocarbamate, methylene bisdioctyldithiocarbamate and methylene bistricycldithiocarbamate.

Ester Compound Having Disulfide Structure

[0053] Examples of the ester compound having a disulfide structure include a disulfide compound represented by the following formula (5) and a compound represented by the following formula (6).



[0054] In the formula (5), R^5 and R^6 each independently represent a hydrocarbyl group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, more preferably 2 to 18 carbon atoms, particularly preferably 3 to 18 carbon atoms. The hydrocarbyl group may have a linear, branched or cyclic structure and may contain an oxygen atom, sulfur atom or nitrogen atom. R^5 and R^6 may be mutually the same or different, but are preferably the same in terms of manufacturing reasons.

[0055] Next, A^1 and A^2 each independently represent a group represented by CR^7R^8 or $CR^7R^8-CR^9R^{10}$, in which R^7 to R^{10} each independently represent a hydrogen atom or a hydrocarbyl group having 1 to 20 carbon atoms. The hydrocarbyl group is preferably one having 1 to 12 carbon atoms, more preferably one having 1 to 8 carbon atoms. A^1 and A^2 may be mutually the same or different, but are preferably the same in terms of manufacturing reasons.

[0056] On the other hand, in the formula (6), R^{11} , R^{12} , R^{16} and R^{17} each independently represent a hydrocarbyl group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, more preferably 2 to 18 carbon atoms, particularly preferably 3 to 18 carbon atoms. The hydrocarbyl group may have a linear, branched or cyclic structure and may contain an oxygen atom, sulfur atom or nitrogen atom. R^{11} , R^{12} , R^{16} and R^{17} may be mutually the same or different, but are preferably the same in terms of manufacturing reasons.

[0057] Next, R^{13} to R^{15} and R^{18} to R^{20} each independently represent a hydrogen atom or a hydrocarbyl group having 1 to 5 carbon atoms. A hydrogen atom is preferable because materials are easily available.

[0058] Examples of the disulfide compound represented by the formula (5) include bis(methoxycarbonylmethyl)disulfide, bis(ethoxycarbonylmethyl)disulfide, bis(n-propoxycarbonylmethyl)disulfide, bis(isopropoxycarbonylmethyl)disulfide, bis(cyclopropoxycarbonylmethyl)disulfide, 1,1-bis(1-methoxycarbonylethyl)disulfide, 1,1-bis(1-methoxycarbonyl-n-propyl)disulfide, 1,1-bis(1-methoxycarbonyl-n-butyl)disulfide, 1,1-bis(1-methoxycarbonyl-n-hexyl)disulfide, 1,1-bis(1-methoxycarbonyl-n-octyl)disulfide, 2,2-bis(2-methoxycarbonyl-n-propyl)disulfide, alpha,alpha-bis(alpha-methoxycarbonylbenzyl)disulfide, 1,1-bis(2-methoxycarbonylethyl)disulfide, 1,1-bis(2-ethoxycarbonylethyl)disulfide, 1,1-bis(2-n-propoxycarbonylethyl)disulfide, 1,1-bis(2-isopropoxycarbonylethyl)disulfide, 1,1-bis(2-cyclopropoxycarbonylethyl)disulfide, 1,1-bis(2-methoxycarbonyl-n-propyl)disulfide, 1,1-bis(2-methoxycarbonyl-n-butyl)disulfide, 1,1-bis(2-methoxycarbonyl-n-hexyl)disulfide, 1,1-bis(2-methoxycarbonyl-n-propyl)disulfide, 2,2-bis(3-methoxycarbonyl-n-pentyl)disulfide, and 1,1-bis(2-methoxycarbonyl-1-phenylethyl)disulfide.

[0059] Examples of the disulfide compound represented by the formula (6) include dimercaptosuccinic acid tetramethyl, dimercaptosuccinic acid tetraethyl, dimercaptosuccinic acid tetra-1-propyl, dimercaptosuccinic acid tetra-2-propyl, dimercaptosuccinic acid tetra-1-butyl, dimercaptosuccinic acid tetra-2-butyl, dimercaptosuccinic acid tetraisobutyl, dimercaptosuccinic acid tetra-1-hexyl, dimercaptosuccinic acid tetra-1-octyl, dimercaptosuccinic acid tetra-1-(2-ethyl)hexyl, dimercaptosuccinic acid tetra-1-(3,5,5-trimethyl)hexyl, dimercaptosuccinic acid tetra-1-decyl, dimercaptosuccinic acid tetra-1-dodecyl, dimercaptosuccinic acid tetra-1-hexadecyl, dimercaptosuccinic acid tetra-1-octadecyl, dimercaptosuccinic acid tetrabenzyl, dimercaptosuccinic acid tetra-alpha-(methyl)benzyl, dimercaptosuccinic acid tetra alpha,alpha-dimethylbenzyl, dimercaptosuccinic acid tetra-1-(2-methoxy)ethyl, dimercaptosuccinic acid tetra-1-(2-ethoxy)ethyl, dimercaptosuccinic acid tetra-1-(2-butoxy)ethyl, dimercaptosuccinic acid tetra-1-(2-ethoxy)ethyl, dimercaptosuccinic acid tetra-1-(2-butoxy-butoxy)ethyl, and dimercaptosuccinic acid tetra-1-(2-phenoxy)ethyl.

Other Sulfur Compounds

[0060] Examples of other sulfur compounds include sulfurized fats and oils such as sulfurized lard, sulfurized rape seed oil, sulfurized castor oil, sulfurized soybean oil and sulfurized rice bran oil; sulfurized fatty acids such as thioglycolic acid and sulfurized oleic acid; dialkyl thiodipropionate compounds such as dilauryl thiodipropionate, distearyl thiodipropionate and dimyristyl thiodipropionate; and thioterpene compounds obtained by reacting phosphorus pentasulfide with pinene.

[0061] The above component (D-1) may be provided using one of the above sulfur compounds alone or using a combination of two or more thereof. The content of the component (D-1) is preferably in a range from 0.2 mass% to 0.6 mass% of the total amount of the composition in terms of the amount of sulfur. The content less than 0.2 mass% is likely to provide an insufficient seizure resistance. On the other hand, the content more than 0.6 mass% is likely to not only deteriorate fatigue resistance such as FZG micropitting resistance but also generate a lot of sludge in the oxidation stability test (in accordance with ASTM D 2893). The content of the component (D-1) is preferably in a range from 0.3 mass% to 0.5 mass%.

[0062] In blending the above component (D-1), preferably, the trihydrocarbyl thiophosphate represented by the formula (2) is also blended as the component (D-2) as desired.

[0063] In the formula (2), R represents a hydrocarbyl group having 6 to 20 carbon atoms. The hydrocarbyl group is a linear, branched or cyclic alkyl group or alkenyl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms. In the aryl group and aralkyl group, one or more alkyl group(s) may be introduced into an aromatic ring. The three RO groups may be mutually the same or different.

[0064] Examples of the alkyl group and alkenyl group each having 6 to 20 carbon atoms include various hexyl groups, various octyl groups, various decyl groups, various dodecyl groups, various tetradecyl groups, various hexadecyl groups, various octadecyl groups, cyclohexyl group, various hexenyl groups, various octenyl groups, various decenyl groups, various dodecenyl groups, various tetradecenyl groups, various hexadecenyl groups, various octadecenyl groups and cyclohexenyl group.

[0065] Examples of the aryl group having 6 to 20 carbon atoms include phenyl group, tolyl group, xylyl group, decyl-phenyl group, 2,4-didecylphenyl group and naphthyl group. Examples of the aralkyl group having 7 to 20 carbon atoms include benzyl group, phenethyl group, naphthylmethyl group, methylbenzyl group, methylphenethyl group and methylnaphthylmethyl group.

[0066] Examples of the trihydrocarbyl thiophosphate represented by the above formula (2) include trihexyl thiophosphate, tri(2-ethylhexyl) thiophosphate, tris(decyl) thiophosphate, trilauryl thiophosphate, trimyristyl thiophosphate, tripalmityl thiophosphate, tristearyl thiophosphate, trioleyl thiophosphate, tricresyl thiophosphate, trixylyl thiophosphate, tris(decylphenyl) thiophosphate and tris[2,4-isoalkyl(C9, C10)phenyl]thiophosphate. One of the above examples of the trihydrocarbyl thiophosphate may be used alone or, alternatively, two or more thereof may be used in combination.

[0067] The trihydrocarbyl thiophosphate as the component (D-2) is blended as desired in order to enhance the effect provided by adding the sulfur compound of the above component (D-1). The content of the trihydrocarbyl thiophosphate is preferably in a range from 0.1 mass% to 1 mass% of the total amount of the composition in terms of the amount of sulfur, more preferably in a range from 0.2 mass% to 0.5 mass%.

[0068] As long as an object of the invention is not impaired, the composition may contain, as required, at least one additive selected from various additives such as an ashless detergent dispersant, antioxidant, rust inhibitor, metal deactivator, viscosity index improver, pour point depressant and antifoaming agent.

[0069] Examples of the ashless detergent dispersant include succinimides, boron-containing succinimides, benzylamines, boron-containing benzylamines, succinic acid esters, and mono- or di-carboxylic acid amides respectively represented by a fatty acid or succinic acid. A content of the ashless detergent dispersant is approximately in a range from 0.01 mass% to 5 mass% of the total amount of the composition in view of a balance between the resulting effect and economic efficiency and the like.

[0070] As the antioxidant, an aminic antioxidant, phenolic antioxidant and sulfuric antioxidant, which are typically used in a lubricating oil, are usable. One of the above antioxidants may be used alone or, alternatively, two or more thereof may be used in combination. Examples of the aminic antioxidant include monoalkyldiphenylamine compounds such as mono-octyldiphenylamine and monononyldiphenylamine; dialkyldiphenylamine compounds such as 4,4'-dibutyldiphenylamine, 4,4'-dibenzoyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine and 4,4'-dinonyldiphenylamine; polyalkyldiphenylamine compounds such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine and tetranonyldiphenylamine; and naphthylamine compounds such as alpha-naphthylamine, phenyl-alpha-naphthylamine, butylphenyl-alpha-naphthylamine, benzylphenyl-alpha-naphthylamine, hexylphenyl-alpha-naphthylamine, heptylphenyl-alpha-naphthylamine, octylphenyl-alpha-naphthylamine and nonylphenyl-alpha-naphthylamine.

[0071] Examples of the phenolic antioxidant include: monophenol compounds such as 2,6-di-tert-butyl-4-methylphenyl, 2,6-di-tert-butyl-4-ethylphenyl and octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; and diphenol compounds such as 4,4'-methylenebis(2,6-di-tert-butylphenol) and 2,2'-methylenebis(4-ethyl-6-tert-butylphenol).

[0072] Examples of sulfuric antioxidant include: 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazine-2-ylamino)phenol; thioterpenes compounds such as a reactant of phosphorus pentasulfide and pinene; and dialkyl thiodipropionates such as dilauryl thiodipropionate and distearyl thiodipropionate.

[0073] A content of the antioxidant is approximately in a range from 0.3 mass% to 2 mass% of the total amount of the composition in view of a balance between the resulting effect and economic efficiency and the like.

[0074] Examples of the rust inhibitor include metal sulfonate and alkenyl succinic acid ester. A content of the rust inhibitor is approximately in a range from 0.01 mass% to 0.5 mass% in view of the blending effect thereof.

[0075] Examples of the metal deactivator (copper corrosion inhibitor) include benzotriazole compounds, tolyltriazole compounds, thiadiazole compounds, imidazole compounds and pyrimidine compounds. Among the above, the benzotriazole compounds are preferable. A content of the metal deactivator is approximately in a range from 0.01 mass% to 0.1 mass% in view of the blending effect thereof.

[0076] Examples of the viscosity index improver include polymethacrylate, dispersed polymethacrylate, olefin copolymer (e.g. ethylene-propylene copolymer), dispersed olefin copolymer and styrene copolymer (e.g. styrene-diene copolymer and styrene-isoprene copolymer). A content of the viscosity index improver is approximately in a range from 0.5 mass% to 15 mass% in view of the blending effect thereof.

[0077] Examples of the pour point depressant include an ethylene-vinyl acetate copolymer, condensate of chlorinated paraffin and naphthalene, condensate of chlorinated paraffin and phenol, polymethacrylate and polyalkylstyrene, among which polymethacrylate having a mass average molecular weight of approximately 50000 to 150000 is preferably used. A content of the pour point depressant is approximately in a range from 0.1 mass% to 5 mass% of the total amount of

the composition.

[0078] The antifoaming agent is preferably a silicone polymer antifoaming agent and a polyacrylate antifoaming agent. By blending the silicone polymer antifoaming agent and the like, antifoaming capabilities can be effectively exhibited. Examples of the silicone polymer antifoaming agent include organopolysiloxanes, among which, in particular, a fluorine-containing organopolysiloxane such as trifluoropropylmethyl silicone oil is suitable. A content of the antifoaming agent is approximately in a range from 0.005 mass% to 0.1 mass% of the total amount of the composition in view of a balance between the resulting antifoaming effect and economic efficiency and the like.

[0079] The biodegradable lubricating oil composition according to the exemplary embodiment is excellent in lubricity, low-temperature fluidity, oxidation stability and biodegradability, and thus can be suitably used as various lubricating oils such as a gear oil and a bearing oil. In particular, the composition is suitable as a lubricating oil used for a power transmission device with a planet gear (i.e., step-up gear) disposed in a wind power generator, which is intended to be continuously used outside for a long time. Moreover, when a wind power generator is set on the ocean, in the mountain or the like, the composition is particularly suitable as a lubricating oil used for a step-up gear disposed in the wind power generator.

Examples

[0080] Examples of the invention will be described below further in detail. However, it should be noted that the scope of the invention is by no means limited by the examples.

Examples 1 to 3, Comparatives 1 to 3

[0081] Various ester base oils were blended with various additives, and the resulting lubricating oil compositions (sample oils) were evaluated in various aspects.

[0082] Details of various components used as base oils and various additives are shown below. The properties of carboxylates are shown in Table 1.

Table 1

	Kinematic Viscosity at 40 degrees C (mm ² /s)	Acid Value (mgKOH/g)	Saponification Value (mgKOH/g)	Biodegradation Rate (%)
Ester A (component A)	538.8	0.16	395	50
Ester B (component A)	550.8	0.13	406	50
Ester C (component A)	558.8	0.13	406	51
Ester D	549.7	0.12	393	50
Ester E	492.7	0.12	222	52
Ester F (component B)	33.5	0.04	287	88
Ester G	105.0	0.06	176	65

(1) Ester A (Component A)

[0083] An ester A was provided by a complex ester (KAOLUBE 150-28 manufactured by Kao Corporation) that was formed from caprylic acid, capric acid, adipic acid and trimethylolpropane at 6:4 of a molar ratio (C8:C10) between the caprylic acid (C8) and capric acid (C10).

(2) Ester B (Component A)

[0084] An ester B was provided by a complex ester (KAOLUBE 150-30 manufactured by Kao Corporation) that was formed from caprylic acid, capric acid, adipic acid and trimethylolpropane at 8:2 of a molar ratio (C8:C10) between the caprylic acid (C8) and capric acid (C10).

(3) Ester C (Component A)

[0085] An ester C was provided by a complex ester (KAOLUBE 150-31 manufactured by Kao Corporation) that was formed from caprylic acid, capric acid, adipic acid and trimethylolpropane at 9:1 of a molar ratio (C8:C10) between the caprylic acid (C8) and capric acid (C10).

(4) Ester D

[0086] An ester D was provided by a complex ester (KAOLUBE 150-29 manufactured by Kao Corporation) that was formed from caprylic acid, capric acid, adipic acid and trimethylolpropane at 5:5 of a molar ratio (C8:C10) between the caprylic acid (C8) and capric acid (C10).

(5) Ester E

[0087] An ester E was provided by a complex ester (PRIOLUBE 1851 manufactured by Uniqema Ltd.) that was formed from pentaerythritol, sebacic acid and isostearic acid.

(6) Ester F (Component B)

[0088] An ester F was provided by an ester formed from pentaerythritol and saturated fatty acid (KAOLUBE 262 manufactured by Kao Corporation).

(7) Ester G

[0089] An ester G was provided by trimethylolpropane diisostearate.

(8) PAO

[0090] PAO was provided by poly- α -olefin (PA040 manufactured by INEOS U.S.A. LLC).

(9) Phosphate Amine Salt (Component C)

[0091] Tridecyl acid phosphate and trioctylamine were used.

(10) Sulfur Compound (Component D)

[0092] Methylene bisdibutyldithiocarbamate and tris(2,4-C9-C10 isoalkylphenol)thiophosphate were used.

(11) Antioxidant

[0093] IRGANOX L 107 manufactured by Ciba Specialty Chemicals Inc. was used as a phenolic antioxidant. IRGANOX L57 manufactured by Ciba Specialty Chemicals Inc. was used as an aminic antioxidant.

(12) Metal Deactivator

[0094] IRGAMET39 (a benzotriazole derivative) manufactured by Ciba Japan K.K. was used.

(13) Antifoaming Agent

[0095] A silicone antifoaming agent (KF96H12500CS manufactured by Shin-Etsu Chemical Co., Ltd.) was used.

(14) Anti-emulsifier

[0096] LUBRIZOL 5957 (PAG-based) manufactured by Lubrizol Co., Ltd. was used.

[0097] Properties-measurement methods and evaluation methods for base oils and sample oils were as follows. Table 2 shows evaluation results of sample oils (biodegradability, oxidation stability, lubricity).

EP 2 752 480 A1

(1) Kinematic Viscosity

[0098] A kinematic viscosity was measured by a method in accordance with JIS K 2283.

(2) Acid Value

[0099] An acid value was measured by a method in accordance with JIS K 2501.

(3) Saponification Value

[0100] A saponification value was measured by a method in accordance with JIS K 2503.

(4) Sulfur Content

[0101] A sulfur content was measured by a method in accordance with JIS K 2541.

(5) Phosphorus Content

[0102] A phosphorus content was measured by a method in accordance with ASTM D 5185.

(6) Biodegradability

[0103] A biodegradation rate was measured in accordance with a modified MITI test method (OECD301C). According to the authorized standard of ECOMARK revised in July, 1998, a biodegradation rate is required to be 60% or more.

(7) Oxidation Stability Test

[0104] In accordance with ASTM D 2893, each of the sample oils was oxidized with air under predetermined conditions (121 degrees C, 312 hours), and then an increasing rate of a kinematic viscosity at 100 degrees C, an increasing amount of an acid value, and an amount of sludge after filtration by a millipore filter were measured.

(8) Pour Point

[0105] A pour point was measured by a method in accordance with JIS K2269.

(9) Lubricity

[0106] Using a ball-on-disc tester and under measurement conditions described in DIN51834, friction coefficients after the elapse of 15 minutes, 30 minutes, 90 minutes and 120 minutes after a test for each of the sample oils was started were measured.

Table 2

			Example 1	Example 2	Example 3	Comparative 1	Comparative 2	Comparative 3	
Blending composition (mass%)	Base Oils	Ester A (Component A)	79.0	—	—	—	—	—	
		Ester B (Component A)	—	78.5	—	—	—	—	
		Ester C (Component A)	—	—	78.5	—	—	—	
		Ester D	—	—	—	78.5	—	—	
		Ester E	—	—	—	—	80.2	—	
		Ester F (Component B)	17.2	17.7	17.7	17.7	16.0	—	
		Ester G	—	—	—	—	—	10.0	
		PAO	—	—	—	—	—	86.2	
	Additives	phosphate amine salt (Component C)	tridecyl acid phosphate	0.27	0.27	0.27	0.27	0.27	0.27
			trioctyl amine	0.32	0.32	0.32	0.32	0.32	0.32
		sulfur compound (Component D)	dithiocarbamate	1.65	1.65	1.65	1.65	1.65	1.65
			thiophosphate	0.40	0.40	0.40	0.40	0.40	0.40
		antioxidant	phenolic antioxidant	0.50	0.50	0.50	0.50	0.50	0.50
			aminic antioxidant	0.50	0.50	0.50	0.50	0.50	0.50
		metal deactivator	benzotriazole derivative	0.05	0.05	0.05	0.05	0.05	0.05
		antifoaming agent	silicone antifoaming agent	0.10	0.10	0.10	0.10	0.10	0.10
	anti-emulsifier	PAG	0.01	0.01	0.01	0.01	0.01	0.01	
element content (mass ppm)		phosphorus content	424	416	420	415	397	400	
		sulfur content	5100	5100	5100	5100	5100	5100	
Evaluation Results	biodegradability (biodegradation rate %)		66	66	67	66	67	6	
	oxidation stability test	viscosity increasing rate @ 100 degrees C (%)	2.3	2.3	2.6	2.3	3.8	1.6	
		increasing amount of acid value (mgKOH/g)	-0.11	-0.08	-0.13	-0.10	0.07	0.01	
		residual amount after filtration (mg/100ml)	0.0	0.0	0.0	52.0	0.2	0.0	
	pour point (°C)		-42.5	-42.5	-42.5	-45.0	-35.0	-42.5	
	lubricity (DIN51834)	f15	0.129	0.117	0.104	0.114	0.111	0.113	
		f30	0.135	0.110	0.100	0.104	0.118	0.111	
		f90	0.117	0.103	0.099	0.098	0.098	0.106	
		f120	0.106	0.100	0.100	0.095	0.096	0.107	
Wk (mm)		0.946	0.799	0.730	0.811	0.765	0.535		

Evaluation Results

[0107] As shown in Table 2, the sample oils of Examples 1 to 3, which satisfy the conditions of the invention, are excellent in all of lubricity, low-temperature fluidity, oxidation stability and biodegradability. Thus, it is understandable that these sample oils exhibit excellent properties as, for instance, an oil for a step-up gear used in a wind power generator. On the other hand, since the ester D (base oil) for the sample oil of Comparative 1 is formed at 5:5 of a molar ratio (C8:C10) between caprylic acid (C8) and capric acid (C10), the sample oil of Comparative 1 exhibits a poor oxidation stability. Moreover, since the ester E (base oil) for the sample oil of Comparative 2 has a structure having a fatty acid different from that of the ester A, the sample oil of Comparative 2 exhibits a poor low-temperature fluidity. The sample oil of Comparative 3 is provided by blending PAO (base oil) and, further, 10 mass% of the ester G (branched aliphatic carboxylic acid polyhydric alcohol ester). The sample oil of Comparative 3 exhibits a poor biodegradability.

Claims

1. A biodegradable lubricating oil composition comprising:

5 a component (A) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid and a linear aliphatic dicarboxylic acid with a polyhydric alcohol, the ester having a kinematic viscosity at 40 degrees C in a range from 400 mm²/s to 1000 mm²/s and an acid value of 0.5 mgKOH/g or less;
 a component (B) that is an ester obtained by reacting a linear saturated aliphatic carboxylic acid with a polyhydric alcohol, the ester having an acid value of 0.5 mgKOH/g or less; and
 10 a component (C) that is a phosphate amine salt obtained by reacting an acidic phosphate with an alkylamine, wherein
 the linear saturated aliphatic carboxylic acid in the component (A) is formed of a linear saturated aliphatic carboxylic acid having 8 carbon atoms and a linear saturated aliphatic carboxylic acid having 10 carbon atoms, and
 15 a molar amount of the linear saturated aliphatic carboxylic acid having 8 carbon atoms is larger than a molar amount of the linear saturated aliphatic carboxylic acid having 10 carbon atoms.

2. The biodegradable lubricating oil composition according to claim 1, wherein
 the linear saturated aliphatic carboxylic acid in the component (A) is formed of the linear saturated aliphatic carboxylic acid having 8 carbon atoms in a range from 60 mol% to 90 mol% and the linear saturated aliphatic carboxylic acid having 10 carbon atoms in a range from 10 mol% to 40 mol%.

3. The biodegradable lubricating oil composition according to claim 1 or 2, wherein
 the biodegradable lubricating oil is a gear oil or a bearing oil.

4. The biodegradable lubricating oil composition according to claim 3, wherein
 the gear oil is used for a step-up gear of a wind power generator.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/072011

A. CLASSIFICATION OF SUBJECT MATTER

C10M169/04(2006.01)i, C10M105/38(2006.01)i, C10M105/42(2006.01)i,
C10M137/08(2006.01)i, C10N20/00(2006.01)n, C10N20/02(2006.01)n,
C10N30/00(2006.01)n, C10N30/02(2006.01)n, C10N30/06(2006.01)n,
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M169/04, C10M105/38, C10M105/42, C10M137/08, C10N20/00, C10N20/02,
C10N30/00, C10N30/02, C10N30/06, C10N30/10, C10N40/02, C10N40/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012
Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2010-260972 A (Idemitsu Kosan Co., Ltd.), 18 November 2010 (18.11.2010), paragraphs [0004] to [0058] & EP 2428552 A1 & WO 2010/128658 A1 & CN 102421881 A	1-4
Y	JP 2003-226886 A (Henkel Corp.), 15 August 2003 (15.08.2003), paragraph [0023]; examples & US 6656888 B1 & EP 656931 A1 & WO 1994/005745 A1 & NO 950755 A & NZ 255727 A & AU 7027096 A & CA 2142608 A & MX 9305226 A & KR 10-0245894 B & CN 1083856 A & AU 688696 B & TW 408172 B	1-4

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
12 November, 2012 (12.11.12)

Date of mailing of the international search report
20 November, 2012 (20.11.12)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/072011

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 8-500627 A (Henkel Corp.), 23 January 1996 (23.01.1996), page 16, lines 8 to 12; examples & US 6656888 B1 & EP 656931 A1 & WO 1994/005745 A1 & NO 950755 A & NZ 255727 A & AU 7027096 A & CA 2142608 A & MX 9305226 A & KR 10-0245894 B & CN 1083856 A & AU 688696 B & TW 408172 B	1-4
Y	JP 2006-274036 A (Nippon Oil Corp.), 12 October 2006 (12.10.2006), paragraph [0119] (Family: none)	1-4
A	JP 2008-274190 A (Cosmo Oil Lubricants Co., Ltd.), 13 November 2008 (13.11.2008), paragraphs [0009] to [0066] (Family: none)	1-4
A	JP 2008-088301 A (Cosmo Oil Lubricants Co., Ltd.), 17 April 2008 (17.04.2008), paragraphs [0008] to [0048] (Family: none)	1-4
A	JP 2002-530476 A (Exxonmobil Chemical Patents Inc.), 17 September 2002 (17.09.2002), paragraphs [0009] to [0078] & EP 1141178 A1 & WO 2000/029521 A1 & AU 1625100 A & BR 9915399 A & CA 2350768 A & CN 1332785 A	1-4
A	JP 2001-234183 A (New Japan Chemical Co., Ltd.), 28 August 2001 (28.08.2001), paragraphs [0009] to [0092] (Family: none)	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/072011

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C10N30/10(2006.01)n, C10N40/02(2006.01)n, C10N40/04(2006.01)n

(According to International Patent Classification (IPC) or to both national
classification and IPC)

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

- JP 2003522204 A [0005]
- JP 2005520038 A [0005]
- JP 2010260972 A [0005]