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(71) Applicant: **NOF Corporation**

**Shibuya-ku**

**Tokyo 150-6019 (JP)**

(72) Inventors:

- **MONJIYAMA, Shunsuke**  
**Amagasaki-shi Hyogo 660-0095 (JP)**
- **KAWAMOTO, Hideki**  
**Amagasaki-shi Hyogo 660-0095 (JP)**
- **ODA, Kazuhiro**  
**Amagasaki-shi Hyogo 660-0095 (JP)**

(74) Representative: **Mewburn Ellis LLP**

**Aurora Building**

**Counterslip**

**Bristol BS1 6BX (GB)**

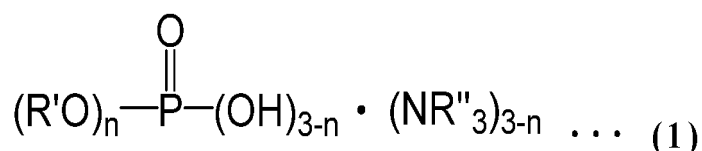
(54) **LUBRICANT COMPOSITION**

(57) [Object] The object is to provide a lubricant oil composition excellent in biodegradability, lubricating property (extreme pressure property), stability against oxidation and demulsibility, having low toxicity and bioaccumulation property in an aquatic life, and excellent in stability against shearing even in the presence of water.

[Solution] A lubricant oil composition comprises 100 mass parts of the following ester compound (A), 0.1 to 1.5 mass parts of the following amine salt (B) of an acidic phosphoric acid ester, 0.3 to 2.0 mass parts of an amine-based oxidation preventing agent (C), and 0.3 to 2.0 mass parts of a phenol-based oxidation preventing agent (D),

(A) the ester compound comprising a molar percentage of 20 to 30 mol% of a constituent component (a) derived from pentaerythritol, a molar percentage of 55 to 79 mol% of a constituent component (b) derived from a straight-chain fatty acid having a carbon number of 14 to 22, and a molar percentage of 1 to 15 mol% of a constituent component (c) derived from adipic acid, wherein a ratio [(c) mol%/(b) mol%] of the molar percentage of the constituent component (b) with respect to the molar percentage of the constituent component (c) is 0.02 to 0.25 and wherein the ester compound has a hydroxyl value of 10 to 100 mgKOH/g,

(B) the amine salt of an acidic phosphoric acid ester represented by the following formula (1),



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(in the formula (1), n represents an integer of 1 or 2, R' represents a straight-chain alkyl group having a carbon number of 4 to 6, and R" represents hydrogen or an alkyl group having a carbon number of 11 to 14.).

**Description**

## TECHNICAL FIELD

**[0001]** The present invention relates to a lubricant oil composition excellent in biodegradability, lubricating property (extreme pressure property), stability against oxidation and demulsibility, low in toxicity to and bioaccumulation property in an aquatic life, and excellent in stability against shearing even in the presence of water. The lubricating oil composition may preferably be applied for a bearing oil, hydraulic oil, gear oil or the like, and may appropriately applied particularly for a stern tube bearing oil, thruster oil or the like used in ocean areas.

## BACKGROUND ARTS

**[0002]** Recently, it is demanded new trials for environmental preservation as important mission worldwide, and in the field of a lubricant oil, it is further demanded a lubricant oil capable of reducing environmental load more than ever. As a lubricant oil capable of reducing the environmental load, a biodegradable lubricant oil draws attention, as the lubricant oil is susceptible to decomposition in natural world to reduce its effects on ecosystem even in the case that the lubricant oil is leaked out.

**[0003]** Various kinds of researches have been made about the biodegradable lubricant oil until now. For example, according to patent document 1, it is disclosed a biodegradable gear oil produced by blending an acidic phosphate ester amine salt into a base oil composed of a complex ester of a polyvalent alcohol and a straight-chain saturated fatty acid and straight-chain divalent fatty carboxylic acid. Further, according to patent document 2, it is disclosed a biodegradable hydraulic oil produced by blending an oxidization preventing agent and load bearing additive into a complex ester of a polyvalent alcohol and a straight-chain fatty acid and straight-chain saturated polycarboxylic acid.

**[0004]** Many of biodegradable lubricant oils have been applied as a countermeasure in the case of leakage into rivers and oceans, and its use is mandatory in some regions and applications. For example, in European countries, the use of the biodegradable lubricant oil is mandated in 2-cycle engine oil in an outboard motor for use in lake regions, hydraulic oil for construction machinery used near a river for taking drinking water, or the like. As such lubricant oil applied in the vicinity of water, for example, according to patent document 3, it is disclosed a biodegradable lubricant oil including a base of (poly)alkylene glycol and which is soluble in water.

[PRIOR TECHNICAL DOCUMENTS]

[PATENT DOCUMENTS]

**[0005]**

[PATENT DOCUMENT 1] Japanese Patent Publication No. 2013-053227 A

[PATENT DOCUMENT 2] Japanese Patent Publication No. 2015-147859 A

[PATENT DOCUMENT 3] Japanese Patent Publication No. 2017-186529 A

## SUMMARY OF THE INVENTION

[OBJECT TO BE SOLVED BY THE INVENTION]

**[0006]** Further, recently in the United States, in a lubricant oil for ships applied for ships moving in water region of the United States, it is mandated a lubricant oil having biodegradability and low toxicity and bioaccumulation property in an aquatic life, and it is demanded a lubricant oil having lower environmental load. Among the above applications, in the stern tube bearing oil, thruster oil or the like, it is difficult to terminate the operation of an equipment directly at the time of contamination of water content, and the equipment may be used for a specific time period while the water content is contaminated therein. Thus, the demulsibility and stability against mechanical shearing force are required even in the state that the water content is incorporated therein.

**[0007]** However, according to the prior techniques described above, the objects described above have not been sufficiently studied, and it is demanded a biodegradable lubricant oil having low toxicity and bio accumulative property in an aquatic life, having demulsibility and excellent in the stability against shearing even in the presence of water.

**[0008]** An object of the present invention is to provide a lubricant oil composition excellent in biodegradability, lubricating property (extreme pressure property), stability against oxidation and demulsibility, having low toxicity and bioaccumulation

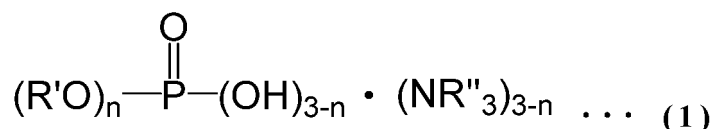
property in an aquatic life, and excellent in stability against shearing even in the presence of water.

# [SOLUTION FOR THE OBJECT]

**[0009]** As the present inventors have extensively researched for solving the objects described above, a specific ester compound (A), of pentaerythritol and a specific straight-chain fatty acid and adipic acid, and a specific acidic phosphoric acid ester amine salt (B) are blended in a specific ratio. It is thus found that it is possible to provide a composition excellent in biodegradability, lubricant property (extreme pressure property), stability against oxidation and demulsibility, having low toxicity and bioaccumulation property in an aquatic life and having excellent stability against shearing even in the presence of water.

**[0010]** That is, the present invention is as follows.

**[0011]** A lubricant oil composition comprising 100 mass parts of the following ester compound (A), 0.1 to 1.5 mass parts of the following amine salt of an acidic phosphoric acid ester (B), 0.3 to 2.0 mass parts of an amine-based oxidation preventing agent (C), and 0.3 to 2.0 mass parts of a phenol-based oxidation preventing agent (D), (A) said ester compound comprising a molar percentage of 20 to 30 mol% of a constituent component (a) derived from pentaerythritol, a molar percentage of 55 to 79 mol% of a constituent component (b) derived from a straight-chain fatty acid having a carbon number of 14 to 22, and a molar percentage of 1 to 15 mol% of a constituent component (c) derived from adipic acid, wherein a ratio [(c) mol%/(b) mol%] of said molar percentage of said constituent component (b) derived from said straight-chain fatty acid with respect to said molar percentage of said constituent component (c) derived from adipic acid is 0.02 to 0.25 and wherein said ester compound has a hydroxyl value of 10 to 100 mgKOH/g, (B): said amine salt of an acidic phosphoric acid ester represented by the following formula (1),



(in the formula (1),

n represents an integer of 1 or 2,

R' represents a straight-chain alkyl group having a carbon number of 4 to 6, and

R'' represents hydrogen or an alkyl group having a carbon number of 11 to 14).

# [EFFECT OF THE INVENTION]

**[0012]** As the lubricant oil composition of the present invention is excellent in biodegradability, lubricating property (extreme pressure property), stability against oxidation and demulsibility, has low toxicity and bioaccumulation property and has excellent stability against shearing even in the presence of water, it can be appropriately applied for a bearing oil, hydraulic oil, gear oil or the like, and may appropriately applied particularly for a stern tube bearing oil, thruster oil or the like used in ocean areas.

# EMBODIMENTS FOR CARRYING OUT THE INVENTION

**[0013]** The lubricant oil composition of the present invention will be described below. Further, a numerical range defined by the symbol "-" in the specification includes numerals at both ends (upper limit and lower limit). For example, "2 to 5" means 2 or more and 5 or less.

**[0014]** The ester compound (A) of the present invention is an ester compound of (a) pentaerythritol, (b) straight-chain fatty acid having a carbon number of 14 to 22 and (c) adipic acid.

**[0015]** As a raw material of the ester compound (A), pentaerythritol is applied due to its excellent stability against oxidation and heat resistance.

**[0016]** The straight-chain fatty acid having a carbon number of 14 to 22 and applied in the ester compound (A) is a straight-chain saturated fatty acid having a carbon number of 14 to 22, a straight-chain unsaturated fatty acid having a carbon number of 14 to 22 or the mixed fatty acids thereof. The straight-chain saturated fatty acid having a carbon number of 14 to 22 may be, for example, myristic acid, palmitic acid, stearic acid, arachidic acid or behenic acid. The straight-chain unsaturated fatty acid having a carbon number of 14 to 22 may be, for example, myristoleic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid or erucic acid. The straight-chain saturated fatty acid and straight-chain unsaturated fatty acid as described above may preferably be palmitoleic acid, oleic acid, linoleic acid, linolenic acid or

erucic acid, more preferably oleic acid, linoleic acid or linolenic acid, and most preferably oleic acid.

**[0017]** In the case that the carbon number of the straight-chain fatty acid is less than 14, the lubricating property (extreme pressure property) may possibly be deteriorated. On the other hand, in the case that the carbon number of the straight-chain fatty acid is more than 22, the fuel efficiency may possibly be deteriorated due to the energy loss caused by the internal resistance of the lubricating oil itself accompanied with a high viscosity, and the generated ester compound becomes solid so that it cannot be possibly applied as a lubricating oil. On such viewpoint, the carbon number of the straight-chain fatty acid may preferably be 16 or more or more preferably be 20 or less. In the mixed fatty acids of the straight-chain saturated fatty acid and straight-chain unsaturated fatty acid each having a carbon number of 14 to 22 (the total content is defined as 100 mass%), the content of the straight-chain unsaturated fatty acid may preferably be 60 mass% or higher, more preferably be 65 mass% or higher and most preferably be 70 mass% or higher.

**[0018]** As the raw material of the ester compound (A), adipic acid is applied as a dibasic acid. In the case that succinic acid or the like with a carbon number less than that of adipic acid is applied, effects may not be exhibited upon the addition of various kinds of additives, so that it may not be suitable as a lubricating base oil. On the other hand, in the case that sebacic acid or the like with a carbon number more than that of adipic acid is applied or that maleic acid or the like including an unsaturated bond is applied, the stability against oxidation or heat resistance may possibly be deteriorated. Thus, adipic acid is preferred as the dibasic acid applied in the present invention.

**[0019]** According to the ester compound (A), the molar percentage of the constituent component (a) derived from pentaerythritol is 20 to 30 mol%, the molar percentage of the constituent component (b) derived from the straight-chain fatty acid having a carbon number of 14 to 22 is 55 to 79 mol%, the molar percentage of the constituent component (c) derived from adipic acid is 1 to 15 mol%, and the ratio [(c)mol%/(b)mol%] of the molar percentage of the constituent component (b) derived from the straight-chain fatty acid having a carbon number of 14 to 22 with respect to the molar percentage of the constituent component (c) derived from adipic acid is 0.02 to 0.25.

**[0020]** The molar percentages of the respective constituent components (a), (b) and (c) derived from the respective raw materials are defined as (a) mol%, (b) mol% and (c) mol%.

(a) mol%, (b) mol%, (c) mol% and [(c) mol%/(b) mol%] are values calculated after the ester compound is analyzed by  $^1\text{H}$  NMR and the molar ratios of the constituent components derived from the respective raw materials are obtained.

**[0021]** The measurement condition of  $^1\text{H}$  NMR are shown below.

(Measurement condition)

#### **[0022]**

Equipment for analysis: "JNM-AL400" manufactured by JEOL Ltd.

Frequency: 400 MHz

Nuclear species:  $^1\text{H}$  NMR

Solvent: deuteriochloroform

Standard substance: Tetramethyl silane (0.00 ppm)

Accumulation count: 16 times

Temperature for measurement: 28 °C

**[0023]** The  $^1\text{H}$  NMR chart of the thus obtained ester by the measurement condition described above is analyzed to calculate the molar ratios.

**[0024]** Specifically, the following four peaks are applied.

Peak (I):

3.40 to 3.70 ppm = (a) hydrogen at  $\alpha$  position of unreacted hydroxy group of pentaerythritol

Peak (II):

4.00 to 4.20 ppm = (a) total of hydrogen atoms at  $\alpha$  position of reacted hydroxy groups of pentaerythritol (total of hydrogens at the peak (I) and hydrogens at the peak (II): 8 counts)

Peak (III):

0.85 to 0.90 ppm = (b) hydrogens connected to the terminal carbons of the straight-chain fatty acid having a carbon number of 14 to 22 (3 counts)

Peak (IV):

2.25 to 2.35 ppm = (c) hydrogens at  $\alpha$  position of carbonyl group of adipic acid (4 counts) and (b) hydrogens at  $\alpha$  position of carbonyl group of the straight-chain fatty acid having a carbon number of 14 to 22 (2 counts)

**[0025]** The integral values of the four peaks described above are calculated as follows to obtain the molar ratios (a) mol, (b) mol and (c) mol of the respective constituent components derived from the respective raw materials.

(a)

$$\text{mol} = (\text{integral value of the peak (I)} + \text{integral value of the peak (II)})/8$$

(b)

$$\text{mol} = \text{integral value of the peak (III)}/3$$

(c)

$$\text{mol} = [\text{integral value of the peak (IV)} - ((b) \text{ mol} \times 2)]/4$$

(a) mol%, (b) mol% and (c) mol% are calculated as follows, based on (a) mol, (b) mol and (c) mol obtained as described above.

(a)

$$\text{mol \%} =$$

$$100 \times (a) \text{ mol} / [(a) \text{ mol} + (b) \text{ mol} + (c) \text{ mol}]$$

(b)

$$\text{mol \%} =$$

$$100 \times (b) \text{ mol} / [(a) \text{ mol} + (b) \text{ mol} + (c) \text{ mol}]$$

(c)

$$\text{mol \%} =$$

$$100 \times (c) \text{ mol} / [(a) \text{ mol} + (b) \text{ mol} + (c) \text{ mol}]$$

**[0026]** Further, the molar ratios of the constituent components can be calculated as follows based on (a) mol%, (b) mol% and (c) mol% described above.

**[0027]** Molar ratio of the constituent component (c) derived from adipic acid with respect to the constituent component (b) derived from the straight-chain fatty acid having a carbon number of 14 to 22 = (c) mol%/(b) mol%

**[0028]** Molar ratio of the constituent component (c) derived from adipic acid with respect to the constituent component (a) derived from pentaerythritol = (c) mol%/(a) mol%

**[0029]** Molar ratio of the constituent component (b) derived from the straight-chain fatty acid having a carbon number of 14 to 22 with respect to the constituent component (a) derived from pentaerythritol = (b) mol%/(a) mol%

**[0030]** According to the ester compound (A), (a) mol%:(b) mol%:(c) mol% = 20 to 30mol%: 55 to 79mol%: 1 to 15 mol%. Further, (a) mol % + (b) mol % + (c)mol % is defined as 100 mol%.

**[0031]** In the case that the ranges are out of the ranges described above, there are possibilities that the rust resistance may be deteriorated, the fuel efficiency may be deteriorated due to energy loss caused by internal resistance of the lubricant oil itself accompanied with a high viscosity, the biodegradability maybe deteriorated and lubricant property (extreme pressure property) may be deteriorated. On such viewpoints, (a) mol% may preferably be 21 to 27 mol% and more preferably be 22 to 25 mol%. Further, (b) mol% may preferably be 60 to 79 mol% and more preferably be 70 to 75 mol%. Further, (c) mol% may preferably be 2 to 10 mol% and more preferably be 3 to 6 mol%.

**[0032]** Further, according to the ester compound (A), (c) mol%/(b) mol% is 0.02 to 0.25. In the case that (c) mol%/(b) mol% is less than 0.02, the rust prevention property may possibly be deteriorated. On the other hand, in the case that (c) mol%/(b) mol% exceeds 0.25, the energy loss due to internal resistance of the lubricant oil itself accompanied with a high viscosity may be larger, so that the fuel efficiency may be deteriorated or biodegradability may be deteriorated.

(c) mol%/(b) mol% may preferably be 0.03 to 0.20 and more preferably be 0.05 to 0.10.

**[0033]** According to the ester compound (A), (c) mol%/(a) mol% may preferably be 0.05 to 0.55. (c) mol%/(a) mol% is made 0.05 or higher, so that the rust preventing property can be further improved. Further, (c) mol%/(a) mol% is made 0.55 or lower, so that the energy loss due to the internal resistance of the lubricant oil itself accompanied with a high viscosity can be prevented to suppress the deterioration of the fuel efficiency and deterioration of biodegradation. On such viewpoint, (c) mol%/(a) mol% may preferably be 0.10 to 0.40 and more preferably be 0.15 to 0.30.

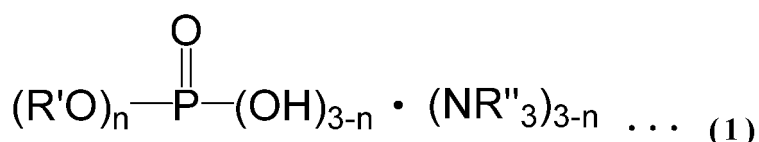
**[0034]** According to the ester compound (A), (b) mol%/(a) mol% may preferably be 2.0 to 4.0. (b) mol%/(a) mol% is made 2.0 or higher, so that the energy loss due to the internal resistance of the lubricant oil itself accompanied with a high viscosity can be suppressed and the deterioration of fuel efficiency due to the internal resistance and deterioration of biodegradability can be suppressed. (b) mol%/(a) mol% may be made 4.0 or higher, so that the rust preventing property can be further improved. On such viewpoints, (b) mol%/(a) mol% may preferably be 2.3 to 3.8 and more preferably be 2.5 to 3.5.

**[0035]** The ester compound (A) has a hydroxyl value of 10 to 100 mgKOH/g. In the case that the hydroxyl value of the ester is lower than 10 mgKOH/g, the rust preventing property may possibly be deteriorated. On the other hand, in the case that the hydroxyl value of the ester exceeds 100 mgKOH/g, the lubricating property (extreme pressure property) or demulsibility may possibly be deteriorated. On such viewpoints, the hydroxyl value of the ester compound (A) may preferably be 15 to 75 mgKOH/g and more preferably be 20 to 60 mgKOH/g.

**[0036]** According to the ester compound (A), the kinetic viscosity at 40°C may preferably be 60 to 300. The kinetic viscosity of the ester at 40°C is made 60 or higher, so that the lubricating property (extreme pressure property) can be further improved. Further, the kinetic viscosity of the ester at 40°C is made 300 or lower, so that the energy loss due to the internal resistance of the lubricating oil itself accompanied with a high viscosity can be reduced and the deterioration of the fuel efficiency can be suppressed. On such viewpoints, the kinetic viscosity of the ester compound (A) at 40°C may preferably be 70 to 200 and more preferably be 75 to 150.

**[0037]** The acid value of the ester compound (A) may preferably be 10.0 mgKOH/g or lower. The acid value of the ester can be made 10.0 mgKOH/g or lower, so that the reduction of lubricating property (extreme pressure property) or stability against oxidation can be suppressed. On such viewpoints, the acid value of the ester compound (A) may preferably be 5.0 mgKOH/g or lower, more preferably be 3.0 mgKOH/g or lower and most preferably be 1.0 mgKOH/g or lower.

**[0038]** Further, the lubricating oil composition of the present invention contains the amine salt of an acidic phosphoric acid ester represented by the following formula.



(n represents an integer of 1 or 2,

R' represents a straight-chain alkyl group having a carbon number of 4 to 6, and

R'' represents hydrogen or an alkyl group having a carbon number of 11 to 14.)

**[0039]** Here, R'' represents hydrogen or a straight-chain or branched-chain alkyl group having a carbon number of 11 to 14. The carbon number of R'' may more preferably be 12 or more and more preferably be 13 or less. At least one of the three R'' may preferably be the straight-chain alkyl group or branched-chain alkyl group having a carbon number of 11 to 14.

**[0040]** According to the amine salt (B) of an acidic phosphoric acid ester, as n represents an integer of 1 or 2, one or two hydroxide groups may be contained. In the case that one hydroxide group is contained, the number of -OR'- group is two, and in the case that two hydroxide groups are contained, the number of -OR'- is one. These may be mixture.

**[0041]** R' represents a straight-chain alkyl group having a carbon number of 4 to 6. In the case that the carbon number of R' is less than 4, sufficient extreme pressure property may not possibly be obtained. Further, in the case that carbon number of R' exceeds 6, sufficient extreme pressure property may not possibly be obtained. According to the present invention, on the viewpoint that excellent lubricating property (extreme pressure property) and stability against oxidation can be obtained, monohexyl or dihexyl phosphate having a carbon number of 6 is most preferred.

**[0042]** R" represents hydrogen or a straight-chain or branched-chain alkyl group having a carbon number of 11 to 14. In the case that the carbon number of R" is 10 or less, as the solubility in the lubricating oil is lowered, so that precipitation or the like may possibly occur at a low temperature upon blending, which is not preferred. On the other hand, in the case that the carbon number of R" is 15 or more, sufficient extreme pressure property may not be obtained. According to the

**[0043]** According to the present invention, 0.1 to 1.5 mass parts of the amine salt (B) of an acidic phosphoric acid ester is contained, with respect to 100 mass parts of the ester compound (A). In the case that the content of amine salt (B) of an acidic phosphoric acid ester is less than 0.1 mass parts, sufficient lubricating property (extreme pressure property) may not possibly be obtained. Further, in the case that the content of the amine salt (B) of an acidic phosphoric acid ester exceeds 1.5 mass parts, the demulsibility may be deteriorated and toxicity in an aquatic life may possibly be increased. On such viewpoints, the content of the amine salt (B) of an acidic phosphoric acid ester may preferably be 0.15 mass parts or higher, more preferably be 1.25 mass parts or higher and most preferably be 1.00 mass parts or lower.

**[0044]** The amine-based oxidation preventing agent (C) may be, for example, phenyl- $\alpha$ -naphthylamine, phenyl- $\beta$ -naphthylamine, alkyl phenyl- $\alpha$ -naphthylamine, alkyl phenyl- $\beta$ -naphthylamine, bis(alkyl phenyl)amine, phenothiazine, monooctyl diphenylamine, 4, 4'-bis( $\alpha$ ,  $\alpha$ - dimethyl benzyl) diphenylamine, 2,2,4-trimethyl-1,2-dihydroquinoline or the polymerized product, 6-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline or the polymerized product, or 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline or the polymerized product, and one kind may be selected or two or more kinds may be selected from the group and may be applied in combination. Among them, on the viewpoint of the improvement of the stability against oxidation together with the application of the amine salt (B) of an acidic phosphoric acid ester, phenyl- $\alpha$ -naphthylamine, phenyl- $\beta$ -naphthylamine, alkyl phenyl- $\alpha$ -naphthylamine, alkyl phenyl- $\beta$ -naphthylamine, bis(alkyl phenyl)amine, monooctyl diphenyl amine and 4, 4'-bis( $\alpha$ ,  $\alpha$ - dimethyl benzyl)diphenylamine are preferred, and phenyl- $\alpha$ -naphthylamine, phenyl- $\beta$ -naphthylamine, alkyl phenyl- $\alpha$ -naphthylamine, alkyl phenyl- $\beta$ -naphthylamine and bis(alkyl phenyl)amine are more preferred.

**[0045]** The content of the amine-based oxidation preventing agent (C) in the lubricating oil composition of the present invention is 0.3 to 2.0 mass parts with respect to 100 mass parts of the ester compound (A). In the case that the content of the amine-based oxidation preventing agent (C) is less than 0.3 mass parts, sufficient stability against oxidation may not possibly be obtained. Further, in the case that the content of the amine-based oxidation preventing agent exceeds 2.0 mass parts, the biodegradability may possibly be deteriorated. On such viewpoints, the content of the amine-based oxidation preventing agent (C) may preferably be 0.5 to 1.5 mass parts and more preferably be 0.6 to 1.0 mass parts.

**[0046]** The phenol-based oxidation preventing agent (D) may be, for example, 2,6-di-*t*-butyl para-cresol, 4,4-methylene bis(2,6-di-*t*-butyl phenol), 4,4-thio bis(2-methyl-6-*t*-butyl phenol), 4,4-bis(2,6-di-*t*-butyl phenol), pentaerythritol tetrakis[3-(3, 5-di-*tert*-butyl-4-hydroxy phenyl)propionate], and one kind or two or more kinds may be selected from the group and applied in combination. The accumulation property in an aquatic life is lower when the phenol-based oxidation preventing agent having a higher molecular weight is applied. On such viewpoint, pentaerythritol tetrakis[3(3, 5-di-*tert*-butyl-4-hydroxy phenyl)propionate] is particularly preferred.

**[0047]** The content of the phenol-based oxidation preventing agent (D) in the lubricating oil composition of the present invention is 0.3 to 2.0 mass parts with respect to 100 mass parts of the ester compound (A). In the case that the content of the phenol-based oxidation preventing agent (D) is less than 0.3 mass parts, sufficient stability against oxidation may not be obtained. Further, the content of the phenol-based oxidation preventing agent (D) exceeds 2.0 mass parts, the biodegradability may possibly be deteriorated. On such viewpoints, the content of the phenol-based oxidation preventing agent (D) may preferably be 0.5 to 1.5 mass parts and more preferably be 0.6 to 1.0 mass parts.

**[0048]** The lubricating oil composition of the present invention may optionally contain known additives for lubricating oil composition for further improving the performance, in addition to the ester compound (A), the amine salt (B) of an acidic phosphoric acid ester, the amine-based oxidation preventing agent (C) and the phenol-based oxidation preventing agent (D). As the additives, a rust-preventing agent, metal deactivator, anti-foaming agent, pour point decreasing agent, viscosity index improver or the like may be optionally and appropriately mixed into the ester and prepared in an amount with the object of the present invention not inhibited. One kind of such additives may be applied alone or two or two or more kinds may be applied in combination.

**[0049]** As the metal inactivator as described above, for example, benzotriazole or the derivative, alkenyl succinic acid ester or the like are listed. These metal deactivators may be applied alone or the two or more kinds may be mixed and applied.

**[0050]** The content of the metal deactivator may preferably be 0.001 to 0.1 mass parts, more preferably be 0.002 to 0.08 mass parts and most preferably be 0.003 to 0.06 mass parts, with respect to 100 mass parts of the ester compound (A).

**[0051]** The rust preventing agent described above may be, for example, alkenyl succinic acid or the derivative, imidazoline derivative such as carboxy imidazoline, oleoyl sarcosine, alkyl phenoxy acetic acid or the like. Such rust preventing agents may be applied alone or the two or more kinds may be mixed and applied. According to the present invention, on the viewpoint of imparting high rust preventing property to the ester compound (A), alkenyl succinic acid

or the derivative is more preferred.

**[0052]** The anti-foaming agent described above may be silicon-based compound or the like.

**[0053]** The lubricating oil composition of the present invention can be produced by blending predetermined amounts of the ester compound (A), the amine salt (B) of an acidic phosphoric acid ester, amine-based oxidation preventing agent (C) and phenol-based oxidation preventing agent, respectively, and optionally by blending the various kinds of the additives described above. The method of the blending, mixing and addition of the respective additives are not particularly limited, and various methods may be applied. The order of the blending, mixing and addition is not particularly limited, and various methods may be applied. For examples, the method of directly adding various kinds of the additives into the ester compound (A) followed by heating and mixing, or the method of preparing solutions of high concentrations of the additives in advance and mixing them with the ester compound (A) may be applied.

## EXAMPLES

**[0054]** The present invention will be described in detail below, referring to the inventive and comparative examples.

(Synthesis of ester compound)

(Synthetic example 1)

**[0055]** Into a 3-liter four-necked flask equipped with a thermometer, nitrogen supply tube, agitator and cooling funnel, 285 g (2.09 mol) of pentaerythritol, 88 g (0.60 mol) of adipic acid, and 1728 g (6.21 mol) of straight-chain fatty acids (myristic acid: 2.0 mass%, myristoleic acid: 1.4 mass%, pentadecenoic acid: 0.2 mass%, palmitic acid: 4.2 mass%, palmitoleic acid: 7.0 mass%, heptadecenoic acid: 1.6 mass%, stearic acid: 1.2 mass%, oleic acid: 73.8 mass%, linoleic acid: 6.7 mass%, linolenic acid: 1.8 mass%, arachidic acid: 0.1 mass%) were charged, followed by the reaction at 240°C at ambient pressure under nitrogen gas flow, while water generated through the reaction was removed. After the reaction product was cooled, 0.5 mass parts of active white clay was added to the reaction product to perform the adsorption, followed by filtration to remove the adsorption agent to obtain the ester compound A1.

(Synthetic example 2)

**[0056]** The charged amounts of the raw materials were changed based on the same procedure as that of the synthetic example 1, to obtain the ester compounds A2 and A'1.

**[0057]** The molar percentages of the components derived from the respective raw materials of the ester compounds A1, A2 and A'1 obtained as above were measured by <sup>1</sup>H NMR and described in table 1. The measurement results of the acid values, hydroxyl values, kinetic viscosities at 40°C, kinetic viscosities at 100°C, viscosity indices and flash points were also described in table 1.

(Inventive examples 1 to 5 and comparative examples 1 to 5)

(Preparation of lubricating oil composition)

**[0058]** The additives were blended into the ester compounds A1, A2 and A'1 obtained as described above according to the following procedure, to prepare the lubricating oil compositions of the inventive examples 1 to 5 and comparative examples 1 to 5.

**[0059]** In a 3-liter four-necked flask equipped with a thermometer, nitrogen supply tube, agitator and cooling funnel, the following additives were added in the blending ratios described in tables 2 and 3 into the ester compounds A1, A2 and A'1 synthesized as above, followed by agitation and mixing at 120°C for 2 hours to obtain lubricating oil compositions.

**[0060]** Further, the following additives were applied.

(Extreme pressure agent)

**[0061]**

(B) mono/di hexyl phosphate-C11 to 14-branched alkyl amine salt (BASF corporation, IRGALUBE 349)

Branched butyl phosphate-C11 to 14 branched alkyl amine salt (LANXESS corporation, RC3740)

Dibenzyl disulfide

(Amine-based oxidation preventing agent)

N-[4-(1,1,3,3-tetramethylbutyl)phenyl]-1-naphthylamine (BASF Corporation, IRGANOX L06)

## EP 4 424 802 A1

(Phenol-based oxidation preventing agent)

Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxy phenyl) propionate] (AntiOx 10 manufactured by NOF corporation) (Metal deactivator)

Benzotriazole derivative (BASF Corporation, IRGAMET39)

(Evaluation of lubricating oil composition)

**[0062]** The following evaluation was made about the thus preped lubricating oil composition as follows, and the results were shown in tables 2 and 3.

(Biodegradability test)

**[0063]** Biodegradability test was performed according to OECD 301C. In the case that the biodegradability measured by the test is 60 percent or higher, it is qualified standards as a biodegradable lubricant oil, according to ECO MARK OFFICE of Public Interest Incorporated foundation "Japan Environment Association". According to this test, it is marked as "Ω" in the case that the biodegradability is 70 percent or higher, it is marked as "O" in the case that the biodegradability is 60 percent or higher and below 70 percent, and it is marked as "×" in the case that the biodegradability is below 60 percent,

(Toxicity and accumulation property in an aquatic life)

**[0064]** The toxicity test in an aquatic life was performed according to OECD 201, 202 and 203. Further, according to OECD117, the test of accumulation property in an aquatic life was performed. According to the test, in the case of the toxicity test, that of EC50 (or LC50)>100mg/L is rated as qualified, and in the case of the accumulation property test, that of log Kow<3 or log Kow>7 was rated as qualified.

**[0065]** As to the evaluation results, that rated as qualified in both tests was represented as "O", and that rated as disqualified in either or both of the tests was represented as "x".

(Stability against oxidation: RPVOT test)

**[0066]** The test of stability against oxidation of the lubricating oil (RPVOT) was performed, based on Japanese industrial standards JIS K2514-3 (2013). As the numerical value described in the table is larger, the oxidation stability is better.

**[0067]** According to the test, "Ω" is described in the case of 150 minutes or more, "O" is described in the case of 100 minutes or more and less than 150 minutes, and "×" is described in the case of less than 100 minutes.

(Shell Four-Ball Load Bearing Capacity Test)

**[0068]** Using a high-speed Shell four-ball testing machine, the maximum non-seizure load was measured according to ASTM D2783. As the maximum non-seizure load described in the table is larger, the extreme pressure property is better.

**[0069]** According to the test, "Ω" is described in the case of 160kgf or larger, "O" is described in the case of 100kgf or larger and less than 160kgf and "×" is described in the case of less than 100kgf.

(Demulsibility)

**[0070]** The test of demulsibility was performed according to Japanese Industrial Standards JIS K 2520. As the emulsified layer is lesser is a shorter time period, the demulsibility becomes better.

**[0071]** According to the test, "Ω" is described in the case that the time period for the emulsified layer reaching 3mL or less is shorter than 30 minutes, "O" is described in the case that the time period is 30 minutes and longer and shorter than 60 minutes, and "×" is described in the case that the time period for the emulsified layer reaching 3mL or less is 60 minutes or longer or that the emulsified layer does not reach 3 ml or less even after 60 minutes or longer.

(Stability against shearing when water is added)

**[0072]** After 10wt% of water was added to the lubricating oil composition, the dependency of viscosity at 40°C on the shearing rate was measured by a rheometer and CP (Cone plate) in a range of 1 to 1,000(1/s). The TI value is calculated as a ratio of the viscosities at shearing rates of 1(1/s) and 100(1/s) [TI value = viscosity at a shearing rate of 100 (1/s) / viscosity at a shearing rate of 1(1/s)]. As the TI value is nearer to 1, the stability against shearing is higher.

**[0073]** According to the test, "O" is described in the case that the TI value is 0.90 or higher, and "×" is described in

the case that the TI value is less than 0.90.

Table 1

|  |                                      | A1    | A2    | A'1   |
|--|--------------------------------------|-------|-------|-------|
| Molar percentage of each constituent component (molar %) | (a) pentaerythritol                  | 23.5  | 25.6  | 31.1  |
|  | (b) oleic acid                       | 69.8  | 61.5  | 62.5  |
|  | (c) adipic acid                      | 6.8   | 12.8  | 6.3   |
| Molar ratio of each constituent component                | (c)mol% / (b)mol%                    | 0.097 | 0.208 | 0.101 |
|  | (c)mol% / (a)mol%                    | 0.29  | 0.50  | 0.20  |
|  | (b)mol% / (a)mol%                    | 2.97  | 2.40  | 2.01  |
| Physical values  | Acid value (mg KOH/g)                | 1.1   | 2.0   | 0.5   |
|  | Hydroxyl value (mg KOH/g)            | 28    | 41    | 132   |
|  | Kinematic viscosity at 40°C (mm2/s)  | 110.4 | 133.2 | 120.0 |
|  | Kinematic viscosity at 100°C (mm2/s) | 17.3  | 19.3  | 16.1  |
|  | Viscosity index                      | 172   | 165   | 144   |
|  | Flash point (°C, COC method)         | 317   | 328   | 326   |

Table 2

|                        |  |   |   | Inventive examples |         |         |         |         |
|------------------------|--|---|---|--------------------|---------|---------|---------|---------|
|                        |  |   |   | 1                  | 2       | 3       | 4       | 5       |
| Base Oil               | Ester compound   |   |   | A1                 | A2      | A1      | A1      | A2      |
|                        | Mass parts   |   |   | 100                | 100     | 100     | 100     | 100     |
| Additives (mass parts) | Extreme pressure agent                                       | (B) mono-diethyl phosphate-C11-14 branched alkyl amine salt |   | 0.5                | 0.5     | 0.5     | 1.2     | 0.2     |
|                        |  | Branched butyl phosphate-C12-14 branched alkyl amine salt   |   | 0                  | 0       | 0       | 0       | 0       |
|                        |  | Dibenzyl disulfide  |   | 0                  | 0       | 0       | 0       | 0       |
|                        | Amine based oxidation preventing agent                       |   | (C) N-[4-(1,1,3,3-tetramethyl butyl) phenyl-1-naphthylamine                     | 0.7                | 1.5     | 0.5     | 0.7     | 0.7     |
|                        | Phenol based oxidation preventing agent                      |   | (D) pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] | 0.7                | 1.5     | 0.5     | 0.7     | 0.7     |
|                        | Metal deactivator  |   | Benzotriazole derivative  | 0.005              | 0.005   | 0.005   | 0.005   | 0.005   |
| Performance            | Biodegradability test  |   |   | Ω                  | O       | Ω       | Ω       | O       |
|                        | Toxicity and accumulation property in aquatic life           |   |   | O                  | O       | O       | O       | O       |
|                        | Stability against oxidation (RPVOT) (minutes)                |   |   | Ω(193)             | Ω(382)  | O(140)  | Ω(231)  | Ω(158)  |
|                        | Extreme pressure property (Seizuer load) (kgf)               |   |   | Ω(160)             | Ω(160)  | Ω(160)  | Ω(200)  | O(126)  |
|                        | Demulsibility  |   |   | Ω                  | Ω       | Ω       | O       | Ω       |
|                        | Stability against shearing upon addition of water (TI value) |   |   | O(0.95)            | O(0.96) | O(0.94) | O(0.98) | O(0.92) |

Table 3

|                        |  |   | Comparative Examples |         |         |         |         |
|------------------------|--|---|----------------------|---------|---------|---------|---------|
|                        |  |   | 1                    | 2       | 3       | 4       | 5       |
| Base Oil               | Ester compound   |   | A'1                  | A1      | A'1     | A2      | A1      |
|                        | Mass parts   |   | 100                  | 100     | 100     | 100     | 100     |
| Additives (mass parts) | Extreme pressure agent                                       | (B)mono-dihexyl phosphate C11-14 branched alkyl amine salt                      | 0.5                  | 2.0     | 0       | 0       | 0.5     |
|                        |  | Branched butyl phosphate-C12-14 branched alkyl amine salt                       | 0                    | 0       | 0.5     | 0       | 0       |
|                        |  | Dibenzyl disulfide  | 0                    | 0       | 0       | 0.5     | 0       |
|                        | Amine based oxidation preventing agent                       | (C) N-[4-(1,1,3,3-tetramethyl butyl) phenyl-1-naphthylamine                     | 0.7                  | 0.7     | 0.7     | 0.7     | 0       |
|                        | Phenol based oxidation preventing agent                      | (D) pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] | 0.7                  | 0.7     | 0.7     | 0.7     | 0       |
|                        | Metal deactivator  | Benzotriazole derivative  | 0.005                | 0.005   | 0.005   | 0.005   | 0.005   |
| Performance            | Biodegradability test  |   | Ω                    | O       | Ω       | O       | Ω       |
|                        | Toxicity and accumulation property in aquatic life           |   | O                    | ×       | O       | O       | O       |
|                        | Stability against oxidation (RPVOT) (minutes)                |   | O(150)               | Ω(268)  | ×(65)   | ×(90)   | ×(21)   |
|                        | Extreme pressure property (Seizure load) (kgf)               |   | O(100)               | Ω(200)  | O(100)  | ×(80)   | Ω(160)  |
|                        | Demulsibility  |   | ×                    | ×       | ×       | Ω       | Ω       |
|                        | Stability against shearing upon addition of water (TI value) |   | O(0.96)              | O(0.99) | ×(0.66) | ×(0.54) | O(0.94) |

**[0074]** As described in the inventive examples 1 to 5 in table 2, by blending the lubricating oil composition of the present invention with the respective additives, the biodegradability, lubricating property (extreme pressure property), stability against oxidation and demulsibility are proved to be excellent, the toxicity and accumulation property in an aquatic life are proved to be low, and the stability against shearing is proved to be excellent even in the presence of water.

**[0075]** As shown in table 3, according to the comparative example 1, the ester compound A'1 is contained instead of the ester compound A1. As the molar percentage of the constituent component (a) is high and the hydroxyl value of the ester compound A'1 is high, the demulsibility of the lubricating oil composition is low.

**[0076]** According to the comparative example 2, as the content of (B) mono-dihexyl phosphate C11-14 branched alkyl amine salt is too high, the toxicity and accumulation property in an aquatic life is high and demulsibility is low.

**[0077]** According to the comparative example 3, as branched butyl phosphate-C12-14 branched alkyl amine salt is contained instead of (B) mono-dihexyl phosphate C11-14 branched alkyl amine salt, the stability against oxidation, demulsibility and stability against shearing upon the addition of water of the lubricant oil composition are low.

**[0078]** According to the comparative example 4, as dibenzyl disulfide is contained instead of (B) mono-dihexyl phosphate C11-14 branched alkyl amine salt, the stability against oxidation, lubricating property (extreme pressure property) and stability against shearing upon the addition of water of the lubricating oil composition are low.

**[0079]** According to the comparative example 5, as the amine-based and phenol-based oxidation preventing agents are not contained, the stability against oxidation of the lubricant oil composition is low.

(Industrial applicability)

**[0080]** The lubricant oil composition of the present invention is excellent in biodegradability, lubricating property (extreme pressure property), stability against oxidation and demulsibility, has low toxicity and accumulation property in an aquatic life and has excellent stability against shearing even in the presence of water. Thus, it can be appropriately applied for a bearing oil, hydraulic oil, gear oil or the like, and may appropriately applied particularly for a stern tube bearing oil, thruster oil or the like used in ocean areas.

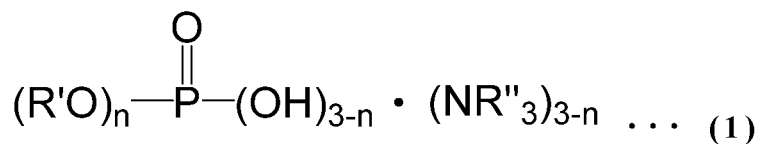
## Claims

1. A lubricant oil composition comprising 100 mass parts of the following ester compound (A), 0.1 to 1.5 mass parts of the following amine salt (B) of an acidic phosphoric acid ester, 0.3 to 2.0 mass parts of an amine-based oxidation preventing agent (C), and 0.3 to 2.0 mass parts of a phenol-based oxidation preventing agent (D),

(A) said ester compound comprising a molar percentage of 20 to 30 mol% of a constituent component (a) derived

from pentaerythritol, a molar percentage of 55 to 79 mol% of a constituent component (b) derived from a straight-chain fatty acid having a carbon number of 14 to 22, and a molar percentage of 1 to 15 mol% of a constituent component (c) derived from adipic acid, wherein a ratio [(c) mol%/(b) mol%] of said molar percentage of said constituent component (b) derived from said straight-chain fatty acid with respect to said molar percentage of said constituent component (c) derived from adipic acid is 0.02 to 0.25 and wherein said ester compound has a hydroxyl value of 10 to 100 mgKOH/g,

(B) said amine salt of an acidic phosphoric acid ester represented by the following formula (1),



(in the formula (1),

n represents an integer of 1 or 2,

R' represents a straight-chain alkyl group having a carbon number of 4 to 6, and

R'' represents hydrogen or an alkyl group having a carbon number of 11 to 14.).

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/038514

| <p><b>A. CLASSIFICATION OF SUBJECT MATTER</b></p> <p><i>C10M 169/04</i>(2006.01)i; <i>C10M 129/10</i>(2006.01)i; <i>C10M 129/78</i>(2006.01)i; <i>C10M 133/12</i>(2006.01)i;<br/> <i>C10M 137/08</i>(2006.01)i; <i>C10N 30/00</i>(2006.01)n; <i>C10N 30/06</i>(2006.01)n; <i>C10N 30/10</i>(2006.01)n; <i>C10N 40/02</i>(2006.01)n;<br/> <i>C10N 40/04</i>(2006.01)n; <i>C10N 40/08</i>(2006.01)n<br/> FI: C10M169/04; C10M129/10; C10M129/78; C10M133/12; C10M137/08; C10N30:00 B; C10N30:00 Z; C10N30:06;<br/> C10N30:10; C10N40:02; C10N40:04; C10N40:08</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>  | <p><b>B. FIELDS SEARCHED</b></p> <p>Minimum documentation searched (classification system followed by classification symbols)</p> <p>C10M169/04; C10M129/10; C10M129/78; C10M133/12; C10M137/08; C10N30/00; C10N30/06; C10N30/10; C10N40/02;<br/> C10N40/04; C10N40/08</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Published examined utility model applications of Japan 1922-1996<br/> Published unexamined utility model applications of Japan 1971-2022<br/> Registered utility model specifications of Japan 1996-2022<br/> Published registered utility model applications of Japan 1994-2022</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p> |  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
|---|---|--|-----------------------|---|--|---|---|---|---|---|--|---|---|---|---|---|--|---|--|
| <p><b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b></p> <table border="1"> <thead> <tr> <th>Category*</th><th>Citation of document, with indication, where appropriate, of the relevant passages</th><th>Relevant to claim No.</th></tr> </thead> <tbody> <tr> <td>Y</td><td>WO 2017/217297 A1 (NOF CORPORATON) 21 December 2017 (2017-12-21)<br/>claims, paragraphs [0002], [0007], [0032], [0036]-[0037], examples 1-7</td><td>1</td></tr> <tr> <td>Y</td><td>US 2017/0121630 A1 (NOVVI LLC) 04 May 2017 (2017-05-04)<br/>paragraph [0132]</td><td>1</td></tr> <tr> <td>A</td><td>JP 2013-53227 A (IDEMITSU KOSAN CO., LTD.) 21 March 2013 (2013-03-21)<br/>in particular, examples 1-3, comparative examples 1-2</td><td>1</td></tr> <tr> <td>A</td><td>JP 2010-260972 A (IDEMITSU KOSAN CO., LTD.) 18 November 2010 (2010-11-18)<br/>in particular, examples 1-2, comparative example 1</td><td>1</td></tr> <tr> <td>A</td><td>JP 8-311472 A (NIPPON OIL CO LTD) 26 November 1996 (1996-11-26)<br/>paragraphs [0043], [0062]</td><td>1</td></tr> </tbody> </table> | Category*   | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. | Y | WO 2017/217297 A1 (NOF CORPORATON) 21 December 2017 (2017-12-21)<br>claims, paragraphs [0002], [0007], [0032], [0036]-[0037], examples 1-7 | 1 | Y | US 2017/0121630 A1 (NOVVI LLC) 04 May 2017 (2017-05-04)<br>paragraph [0132] | 1 | A | JP 2013-53227 A (IDEMITSU KOSAN CO., LTD.) 21 March 2013 (2013-03-21)<br>in particular, examples 1-3, comparative examples 1-2 | 1 | A | JP 2010-260972 A (IDEMITSU KOSAN CO., LTD.) 18 November 2010 (2010-11-18)<br>in particular, examples 1-2, comparative example 1 | 1 | A | JP 8-311472 A (NIPPON OIL CO LTD) 26 November 1996 (1996-11-26)<br>paragraphs [0043], [0062] | 1 | <p><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.</p> <p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“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)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p> <p>“T” 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</p> <p>“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</p> <p>“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</p> <p>“&amp;” document member of the same patent family</p> |
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| Y   | WO 2017/217297 A1 (NOF CORPORATON) 21 December 2017 (2017-12-21)<br>claims, paragraphs [0002], [0007], [0032], [0036]-[0037], examples 1-7  | 1  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| Y   | US 2017/0121630 A1 (NOVVI LLC) 04 May 2017 (2017-05-04)<br>paragraph [0132]   | 1  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| A   | JP 2013-53227 A (IDEMITSU KOSAN CO., LTD.) 21 March 2013 (2013-03-21)<br>in particular, examples 1-3, comparative examples 1-2  | 1  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| A   | JP 2010-260972 A (IDEMITSU KOSAN CO., LTD.) 18 November 2010 (2010-11-18)<br>in particular, examples 1-2, comparative example 1   | 1  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| A   | JP 8-311472 A (NIPPON OIL CO LTD) 26 November 1996 (1996-11-26)<br>paragraphs [0043], [0062]  | 1  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| <p>Date of the actual completion of the international search</p> <p><b>07 November 2022</b></p>   | <p>Date of mailing of the international search report</p> <p><b>22 November 2022</b></p>  |  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |
| <p>Name and mailing address of the ISA/JP</p> <p><b>Japan Patent Office (ISA/JP)</b><br/> <b>3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915</b><br/> <b>Japan</b></p>   | <p>Authorized officer</p> <p>Telephone No.</p>  |  |                       |   |  |   |   |   |   |   |  |   |   |   |   |   |  |   |  |

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| C. DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
| Category*                              | Citation of document, with indication, where appropriate, of the relevant passages        | Relevant to claim No. |
| A                                      | US 2015/0113864 A1 (BASF SE) 30 April 2015 (2015-04-30)<br>in particular, examples 1-8    | 1                     |
| A                                      | JP 6-500577 A (HENKEL CORPORATION) 20 January 1994 (1994-01-20)<br>in particular, table 5 | 1                     |

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**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/JP2022/038514**

| Patent document<br>cited in search report | Publication date<br>(day/month/year) | Patent family member(s)   | Publication date<br>(day/month/year) |
|---|--------------------------------------|---|--------------------------------------|
| WO 2017/217297 A1                         | 21 December 2017                     | US 2019/0241823 A1<br>claims, paragraphs [0002],<br>[0009], [0048], [0053]-[0055],<br>examples 1-7<br>EP 3470498 A1<br>CN 109312245 A<br>KR 10-2019-0018449 A |                                      |
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