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## (54) BIODEGRADABLE LUBRICATING OIL COMPOSITION HAVING FLAME RETARDANCY

(57) The present invention provides a lubricating oil composition exhibiting more excellent flame retardancy and biodegradability.

The biodegradable lubricating oil composition of the invention has flame retardancy and contains (1) a base oil containing a plant-derived oil in an amount of 60 mass% or more, and a polyol ester in an amount of 40 mass% or less, and (2) a polymethacrylate having a mass average molecular weight of 20,000 to 300,000 in an amount of 0.1 to 5 mass%.

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## Description

### Technical Field

**[0001]** The present invention relates to a biodegradable lubricating oil composition having flame retardancy. More particularly, the present invention relates to a biodegradable lubricating oil composition having excellent flame retardancy and high biodegradability, which oil composition is employed as a lubricating oil such as a hydraulic oil or a door closer oil.

### Background Art

**[0002]** Regarding hydraulic oils, many proposals have been made for the purpose of improving flame retardancy. For example, Patent Documents 1 to 4 propose the following hydraulic oils: a self-extinguishing hydraulic oil containing a compound produced through condensation reaction between hexachlorophosphazene, and a perfluoroalkyl alcohol or the like (Patent Document 1); a flame-retardant hydraulic oil containing a polymer compound, the compound containing, as main components, a polyol and a polyol partial ester (Patent Document 2); a flame-retardant hydraulic oil produced by incorporating a high-molecular-weight polymer and a low-molecular-weight polymer into a base oil containing a fatty acid ester or a phosphoric acid ester (Patent Document 3); and a hydraulic fluid composition containing a polyalkylene glycol base fluid, and an alkylene-vinyl ester copolymer which serves as an anti-mist additive and can be dissolved in the base fluid (Patent Document 4). As described in these patent documents, the proposed products exhibit excellent flame retardancy.
When fire occurs, in some cases, a lubricating oil such as a hydraulic oil or a door closer oil employed in a machine may be ejected through a pinhole of the machine and may accelerate the fire. Therefore, demand has arisen for a lubricating oil-such as a hydraulic oil or a door closer oil-which exhibits flame retardancy even in the case of high-pressure spraying or oil leakage. Also, demand has arisen for a lubricating oil composition having higher flame retardancy for improvement of safety, as well as higher biodegradability for reduction of environmental load.

### Prior Art Document

### Patent Document

**[0003]**

Patent Document 1: Japanese Patent No. 2558496
Patent Document 2: Japanese Patent No. 2888742
Patent Document 3: Japanese Patent Application Laid-Open (*kokai*) No. H11-269480
Patent Document 4: Japanese Patent No. 3017803

### Summary of the Invention

### Problems to be Solved by the Invention

**[0004]** As described above, in recent years, lubricating oils have been required to achieve improvement of safety and reduction of environmental load. Therefore, demand has arisen for a lubricating oil composition-such as a hydraulic oil or a door closer oil-which exhibits excellent flame retardancy particularly in the case of leakage of the oil composition, and which has high biodegradability and thus less affects the environment.
In view of the foregoing, an object of the present invention is to provide a lubricating oil composition exhibiting more excellent flame retardancy and biodegradability.

### Means for Solving the Problems

**[0005]** The present invention provides:

[1] a biodegradable lubricating oil composition comprising:

(A) a base oil containing (a) a plant-derived oil in an amount of 60 mass% or more, and (b) a polyol ester in an amount of 40 mass% or less; and
(B) a polymethacrylate having a mass average molecular weight of 20,000 to 300,000 in an amount of 0.1 to 5 mass%;

[2] a biodegradable lubricating oil composition as described in [1] above, wherein the plant-derived oil is rapeseed oil having an oleic acid content of 60 mass% or more;
[3] a biodegradable lubricating oil composition as described in [1] or [2] above, wherein the polyol ester is a polyol partial ester having a hydroxyl value of 30 mg KOH/g or more and a flash point of 300°C or higher;

**[0006]**

[4] a biodegradable lubricating oil composition as described in any of [1] to [3] above, which exhibits a kinematic viscosity at 40°C of 120 $mm^2/s$ or less;
[5] a biodegradable lubricating oil composition as described in any of [1] to [4] above, which is employed as a hydraulic oil, a door closer oil, or a sliding surface oil;
[6] a hydraulic oil comprising a biodegradable lubricating oil composition as recited in any of [1] to [4] above; and
[7] a door closer oil comprising a biodegradable lubricating oil composition as recited in any of [1] to [4] above.

Effects of the Invention

**[0007]** According to the present invention, there can be provided a lubricating oil composition exhibiting more excellent flame retardancy and biodegradability. Best Modes for Carrying Out the Invention

**[0008]** The present invention will next be described in more detail.
The biodegradable lubricating oil composition of the present invention contains (A) a base oil containing (a) a plant-derived oil in an amount of 60 mass% or more, and (b) a polyol ester in an amount of 40 mass% or less; and (B) a polymethacrylate having a mass average molecular weight of 20,000 to 300,000 in an amount of 0.1 to 5 mass%.

[(A) Base oil]

**[0009]** The base oil (A) of the biodegradable lubricating oil composition of the present invention contains (a) a plant-derived oil in an amount of 60 mass% or more, and (b) a polyol ester in an amount of 40 mass% or less.

((a) Plant-derived oil)

**[0010]** The plant-derived oil (a) employed in the base oil may be, for example, rapeseed oil, sunflower oil, soybean oil, corn oil, or canola oil. Particularly, sunflower oil or rapeseed oil is preferably employed, for improvement of, for example, the biodegradability and thermal stability of the lubricating oil composition.

**[0011]** Many plant-derived oils have a total unsaturation degree of more than 0.3. The total unsaturation degree of such an oil can be reduced through hydrogenation or a similar treatment during the process of purifying the oil. Also, a vegetable oil having low total unsaturation degree can be readily produced through a genetic recombination technique. The present invention preferably employs a plant-derived oil having a high oleic acid content, for improvement of, for example, the biodegradability and thermal stability of the lubricating oil composition. For example, the present invention preferably employs a plant-derived oil having an oleic acid content of 60 mass% or more, more preferably a plant-derived oil having an oleic acid content of 70 mass% or more. Examples of preferred plant-derived oils having a high oleic acid content include high oleic canola oil, high oleic rapeseed oil, high oleic sunflower oil, and high oleic soybean oil. High oleic rapeseed oil is particularly preferably employed.
The amount of the aforementioned plant-derived oil contained in the base oil is 60 mass% or more, preferably 70 mass% or more for improvement of biodegradability, more preferably 75 to 99 mass% for improvement of biodegradability and thermal stability.

((b) Polyol ester)

**[0012]** The base oil (A) contains a polyol ester (b) for the purpose of improving the biodegradability and flame retardancy of the lubricating oil composition. No particular limitation is imposed on the polyol ester employed. However, in consideration of the aforementioned purpose, the polyol ester preferably contains, as a main component, a polyol partial ester produced through common esterification reaction between a single polyol and a single chain-form monocarboxylic acid or between two or more polyols and two or more chain-form monocarboxylic acids. The polyol partial ester is produced through esterification of at least a portion of the polyol(s). The percent esterification of the polyol partial ester is preferably 70 to 90%, for improvement of flame retardancy. As used herein, the term "percent esterification" is obtained by dividing the number of esterified hydroxyl groups of a polyol ester by the number of all the hydroxyl groups, inclusive of the esterified hydroxyl groups, of the polyol ester, and is calculated by use of the following formula:

$$\text{Percent esterification (\%)} = \{(SV - AV) \times 100\}/(OHV + SV - AV)$$ (wherein SV represents saponification value, AV represents acid value, and OHV represents hydroxyl value).

**[0013]** Examples of the polyol employed for producing the polyol ester include C3 to C12 polyols having 3 to 6 hydroxyl groups. Specific examples include trivalent alcohols such as glycerin, trimethylolethane, trimethylolpropane, and trimethylolnonane; and polyhydric alcohols such as pentaerythritol, ditrimethylolpropane, dipentaerythritol, sorbitol, and mannitol. Of these, trimethylolpropane, pentaerythritol, and glycerin are preferably employed. These polyols may be employed singly or in combination of two or more species.

**[0014]** Examples of the chain-form monocarboxylic acid employed for producing the polyol ester include C6 to C22 chain-form monocarboxylic acids. Specific examples include straight-chain saturated fatty acids such as caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, arachic acid, and behenic acid; straight-chain unsaturated fatty acids such as undecenoic acid, oleic acid, elaidic acid, setoleic acid, erucic acid, and brassidic acid; and branched-chain saturated fatty acids such as isomyristic acid, isopalmitic acid, isostearic acid, 2,2-dimethylbutanoic acid, 2,2-dimethylpentanoic acid, 2,2-dimethyloctanoic acid, 2-ethyl-2,3,3-trimethylbutanoic acid, 2,2,3,4-tetramethylpentanoic acid, 2,5,5-trimethyl-2-t-butylhexanoic acid, 2,3,3-trimethyl-2-ethylbutanoic acid, 2,3-dimethyl-2-isopropylbutanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid. These chain-form monocarboxylic acids may be employed singly or in combination of two or more species.

**[0015]** In the case of esterification reaction between a polyol and a chain-form monocarboxylic acid, an intended polyol ester can be produced by appropriately regulating the respective amounts of the polyol and chain-form monocarboxylic acid employed. Preferably, light components are sufficiently removed so as not to lower the flash point of the resultant polyol ester. When the resultant polyol ester is employed in the base oil, esterification reaction products may be employed as is, or the respective reaction products may be blended together so as to achieve an intended viscosity.

**[0016]** In the present invention, the polyol ester employed in the base oil preferably has a hydroxyl value of 30 mg KOH/g or more, more preferably 35 mg KOH/g or more. When the hydroxyl value is excessively low, the amount of completely esterified portions increases, and the resultant lubricating oil composition may easily cause continuous combustion as in the case of conventional products. The polyol ester employed in the base oil preferably has a flash point of 300°C or higher. This is because when the flash point is excessively low, ignition is likely to occur.

**[0017]** The polyol ester employed in the present invention preferably has a number average molecular weight of 600 to 1,500, more preferably 600 to 1,000, much more preferably 650 to 950. When the molecular weight is excessively low, the resultant composition may exhibit low viscosity and flash point, and may be readily burned. When the molecular weight is excessively high, the resultant composition may exhibit very high viscosity, and power transmission performance may be lowered. No particular limitation is imposed on the kinematic viscosity of the polyol ester, so long as the viscosity falls within a range corresponding to the intended use of, for example, a hydraulic oil. Generally, the polyol ester preferably exhibits a kinematic viscosity at 40°C of 20 to 200 $mm^2/s$, more preferably 20 to 100 $mm^2/s$, much more preferably 30 to 80 $mm^2/s$, from the viewpoints of pump efficiency and the viscous resistance of the composition in pipes. The polyol ester whose viscosity falls within the aforementioned range is preferably a diester of trimethylolpropane wherein the fatty acid is a mixture of oleic acid and isostearic acid.

The aforementioned polyol ester is incorporated into the base oil in an amount of 40 mass% or less on the basis of the entirety of the base oil. The amount of the polyol ester is preferably 30 mass% or less, more preferably 25 mass% or less, much more preferably 1 to 25 mass%, for improvement of, for example, the flame retardancy, biodegradability, and thermal stability of the lubricating oil composition.

[(B) Polymethacrylate]

**[0018]** In the present invention, the polymethacrylate (B) is employed for the purpose of preventing transformation of the base oil into mist. The polymethacrylate encompasses a methacrylate homopolymer and a methacrylate copolymer. From this viewpoint, the mass average molecular weight of the polymethacrylate is 20,000 to 300,000, preferably 30,000 to 300,000, more preferably 35,000 to 200,000. When the mass average molecular weight is less than 20,000, the aforementioned effects are barely expected, whereas when the mass average molecular weight exceeds 300,000, the resultant composition may be degraded through shearing during use thereof, and the effect of the polymethacrylate may be lowered, resulting in a reduction in viscosity, which is not preferred. The mass average molecular weight of the polymethacrylate may be determined through GPC (gel permeation chromatography) on the basis of the mass average molecular weight as reduced to polystyrene.

**[0019]** In the present invention, the polymethacrylate is incorporated into the lubricating oil composition in an amount of 0.1 to 5 mass%. When the amount of the polymethacrylate is smaller than this range, the effects of the present invention may be lowered, whereas when the amount of the polymethacrylate exceeds this range, the resultant composition is likely to be degraded through shearing, which is not preferred. From the aforementioned viewpoint, the amount of the component (B) incorporated into the lubricating oil composition is preferably 0.1 to 4 mass%, more preferably 0.2 to 3.5 mass%, much more preferably 0.3 to 3.3 mass%.

**[0020]** The base oil (A) employed in the biodegradable lubricating oil composition of the present invention contains the aforementioned plant-derived oil (a) and the aforementioned polyol ester (b). According to the present invention, there can be provided a lubricating oil composition exhibiting more excellent flame retardancy and biodegradability by employing the aforementioned plant-derived oil and polyol ester, and an optimal compound serving as the polymethacrylate; i.e., component (B).

[(C) Additional additive]

**[0021]** Optionally, the biodegradable lubricating oil composition of the present invention preferably contains, an additional additive, at least one species selected from among an antioxidant, a dispersant, a rust-preventive agent, a metal inactivating agent, an oily agent, an extreme pressure agent, a demulsifier, a fluidity-improving agent, and an antifoaming agent, which are generally employed as lubricating oil additives.

Examples of the antioxidant employed in the present invention include phenolic antioxidants such as 2,6-di-t-butyl-4-methylphenol and 4,4'-methylenebis(2,6-di-t-butyl-4-methylphenol); amine antioxidants such as N-phenyl-$\alpha$-naphthylamine, N-phenyl-$\beta$-naphthylamine, phenothiazine, and monooctyldiphenylamine; sulfur-containing antioxidants such as alkyl disulfide and benzothiazole; and zinc dialkyldithiophosphate.

**[0022]** The dispersant employed may be an ashless dispersant and/or a metal-containing detergent. Examples of the ashless dispersant include succinimides, boron-containing succinimides, benzylamines, and boron-containing benzylamines. Examples of the metal-containing detergents include neutral, basic, and perbasic metal sulfonates, metal phenates, metal salicylates, and metal phosphonates. The metal forming such a metal sulfonate, metal phenate, metal salicylate, or metal phosphonate is preferably, for example, an alkaline earth metal such as Ca or Mg. These ashless dispersants or metal-containing detergents may be employed singly or in combination of two or more species.

**[0023]** Examples of the rust-preventive agent include alkenylsuccinic acid, sorbitan monooleate, pentaerythritol monooleate, and amine phosphate. Examples of the metal inactivating agent include benzotriazole, benzothiazole, triazole, dithiocarbamate, imidazole, and derivatives thereof.

Examples of the oily agent include alcohols, fatty acids, and fatty acid esters. Examples of the fatty acid esters include esters formed of a C6 to C22 aliphatic carboxylic acid and a C1 to C18 aliphatic alcohol. Examples of preferred alcohols include C8 to C18 monovalent aliphatic saturated and unsaturated alcohols.

**[0024]** Examples of the extreme pressure agent include zinc dialkyldithiophosphate, dialkyl polysulfide, triaryl phosphate, and trialkyl phosphate.

Examples of the demulsifier include polyoxyalkylene glycol, polyoxyalkylene alkyl ether, polyoxyalkylene alkylamide, and polyoxyalkylene fatty acid ester.

Examples of the fluidity-improving agent include polyalkyl acrylate, alkyl aromatic compounds, and ethylenevinyl acetate copolymers. Examples of the antifoaming agent include dimethylpolysiloxane, diethyl silicate, and ester polymers.

**[0025]** The amount of such an additive incorporated into the lubricating oil composition may be determined in consideration of the intended use of the composition. The total amount of the additive(s) is preferably 5.0 mass% or less, more preferably 3.0 mass% or less, much more preferably 0.5 to 2.5 mass%, on the basis of the entirety of the lubricating oil composition.

[Biodegradable lubricating oil composition]

**[0026]** The biodegradable lubricating oil composition of the present invention contains the base oil (A) containing the plant-derived oil (a) in an amount of 60 mass% or more and the polyol ester (b) in an amount of 40 mass% or less; and the polymethacrylate (B) having a mass average molecular weight of 20,000 to 300,000 in an amount of 0.1 to 5 mass%. The details, amounts, etc. of the respective components have been described above.

**[0027]** The "biodegradability" of the biodegradable lubricating oil composition of the present invention is evaluated through the biodegradability test of chemicals by microorganisms according to OECD Test Guideline 301C. The lubricating oil composition has excellent biodegradability; specifically, the composition exhibits a percent biodegradation of 60% or more, preferably 70% or more, more preferably 80% or more. When the lubricating oil composition is subjected to the acute toxicity test for Japanese killifish according to JIS K 0102, the composition generally exhibits a 96-hour $LC_{50}$ of 100 mg/L or more; i.e., the composition less affects living organisms. Thus, the lubricating oil composition is a very environmentally friendly lubricating oil.

**[0028]** The biodegradable lubricating oil composition of the present invention preferably exhibits a kinematic viscosity at 40°C of 120 $mm^2/s$ or less, more preferably 20 to 80 $mm^2/s$, from the viewpoints of pump efficiency and pipe resistance. The lubricating oil composition preferably exhibits a viscosity index of 130 or more, more preferably 140 or more, for prevention of an increase in viscosity at low temperature. The lubricating oil composition generally exhibits a pour point of -20°C or lower, preferably -30°C or lower, more preferably -35°C or lower, for improvement of low-temperature fluidity. The lubricating oil composition generally exhibits a flash point of 250°C or higher, preferably 260°C or higher, more preferably 300°C or higher, for improvement of flame retardancy. The lubricating oil composition preferably exhibits an acid value of 0.05 to 0.5 mg KOH/g, for improvement of stability.
As described above, the lubricating oil composition exhibits a low pour point. Therefore, when the lubricating oil composition is employed as a hydraulic oil, a door closer oil, or a sliding surface oil, the machine employed exhibits favorable startability at low temperature. Since the lubricating oil composition exhibits a high flash point, it exhibits high flame retardancy. The lubricating oil composition, which exhibits VG32 or more, is classified as a flammable liquid according to the Japanese Fire Services Act, and exhibits excellent safety.

**[0029]** The biodegradable lubricating oil composition of the present invention exhibits excellent biodegradability, less affects living organisms, and exhibits excellent flame retardancy. The lubricating oil composition is suitable for use as, for example, a hydraulic oil employed as a power transmission fluid in a hydraulic system of, for example, a hydraulic machine or apparatus for power transmission, power control, power buffering, etc.; a door closer oil employed for a door closer; i.e., a device which is mounted on a door (hinged door) and automatically closes the opened door; or a sliding surface oil which is applied to various sliding surfaces for imparting lubricity thereto.

## Examples

**[0030]** The present invention will next be described in detail by way of examples, which should not be construed as limiting the invention thereto.

### Examples 1 to 7 and Comparative Examples 1 and 2

**[0031]** A base oil was prepared by mixing a plant-derived oil and a polyol ester in proportions as shown in Table 1. Thereafter, as shown in Table 1, a polymethacrylate and additional additives were added to the base oil, to thereby produce a lubricating oil composition. The thus-produced lubricating oil composition was evaluated in terms of general properties, lubricity, combustibility, and biodegradability as described below. The results are shown in Table 1. Next will be described details of the employed plant-derived oil, polyol esters, and polymethacrylates.

(Plant-derived oil)

**[0032]** High oleic rapeseed oil: amount of oleic acid: 73 mass%, amount of a fatty acid having 16 or less carbon atoms: 4 mass%, amount of a C18 fatty acid (exclusive of oleic acid): 22 mass%

(Polyol ester)

**[0033]**

· TMP (trimethylolpropane) isostearic acid (oleic acid) partial ester: kinematic viscosity at 40°C: 60.0 $mm^2/s$, kinematic viscosity at 100°C: 10.0 $mm^2/s$, acid value as determined through the indicator method: 0.20 mg KOH/g, hydroxyl value: 40.0 mg KOH/g, density (15°C): 0.925 $g/cm^3$, flash point (Cleveland open cup test): 306°C
· PE saturated fatty acid ester: kinematic viscosity at 40°C: 33.5 $mm^2/s$, kinematic viscosity at 100°C: 6.00 $mm^2/s$, acid value as determined through the potential difference method: 0.04 mg KOH/g, hydroxyl value: 2.0 mg KOH/g, density (15°C): 0.961 $g/cm^3$, flash point (Cleveland open cup test): 280°C
· TMP trioleate: kinematic viscosity at 40°C: 49.45 $mm^2/s$, kinematic viscosity at 100°C: 9.81 $mm^2/s$, acid value as determined through the potential difference method: 0.99 mg KOH/g, hydroxyl value: 3.0 mg KOH/g, density (15°C): 0.918 $g/cm^3$, flash point (Cleveland open cup test): 320°C

(Polymethacrylate)

**[0034]**

· PMA (1): acrylic copolymer, kinematic viscosity at 100°C: 835 $mm^2/s$, acid value as determined through the indicator method: 0.05 mg KOH/g, density (15°C): 0.915 $g/cm^3$, mass average molecular weight (Mw): 140,000

- PMA (2): acrylic copolymer, kinematic viscosity at 100°C: 852 $mm^2/s$, acid value as determined through the indicator method: 0.05 mg KOH/g, density (15°C): 0.941 $g/cm^3$, Mw: 37,000
- PMA (3): dispersive acrylic copolymer, kinematic viscosity at 100°C: 1,190 $mm^2/s$, acid value as determined through the indicator method: 0.26 mg KOH/g, density (15°C): 0.906 $g/cm^3$, Mw: 79,000
- PMA (4): alkyl methacrylate copolymer, kinematic viscosity at 100°C: 1,500 $mm^2/s$, density (15°C): 0.933 $g/cm^3$, Mw: 35,000

(Additional additive)

**[0035]**

- Pour-point-improving agent: polyalkyl methacrylate, kinematic viscosity at 100°C: 364.3 $mm^2/s$, acid value as determined through the indicator method: 0.04 mg KOH/g, density (15°C): 0.911 $g/cm^3$

[Evaluation of properties and performances]

(1) Kinematic viscosity

**[0036]** Kinematic viscosity was determined according to JIS K 2283.

(2) Acid value

**[0037]** Acid value was determined through the potential difference method according to the "lubricating oil neutralization test method" specified by JIS K 2501.

(3) Hydroxyl value

**[0038]** Hydroxyl value was determined through the pyridine-acetyl chloride method according to JIS K 0070.

(4) Flash point

**[0039]** Flash point was determined by means of a Cleveland open cup (COC) tester according to JIS K 2274.

(5) Corrosion resistance

**[0040]** The corrosiveness of a sample was evaluated through the test tube method according to JIS K 2513 "Petroleum Products - Corrosiveness to Copper - Copper Strip Test." The test was carried out at 100°C for three hours. The sample copper strip was observed for tarnish with reference to "Copper Strip Corrosion Standards," and a classification number from 1a to 4c was assigned to indicate the degree of corrosiveness. A smaller number represents lower corrosiveness, and corrosiveness increases in alphabetical order.

(6) Rust prevention test

**[0041]** The test was carried out according to JIS K 2510. Specifically, a sample was mixed with water at 60°C, and a test piece of steel round rod was immersed in the mixture for 24 hours. Thereafter, the test piece was observed for determining the presence or absence of rust on the test piece.

(7) Load bearing test

**[0042]** The test was carried out according to ASTM D 2783 at 1,800 rpm and room temperature. Load wear index (LWI) was determined from last non-seizure load (LNL) and weld load (WL). The greater the LWI, the better the load bearing.

(8) Combustibility test

**[0043]** A sample oil sprayed at high pressure was ignited by means of a burner, and preliminarily burned for 10 seconds. Then, the flame of the burner was removed, and the continuous combustion time was measured thereafter. The continuous combustion time was employed as an indicator of flame retardancy. When a sample oil was found to burn continuously for 30 seconds or longer, the test was discontinued at that point in time, and the sample oil was regarded as having "continuous combustibility." Test conditions are as follows: spraying pressure: 70 kg/cm$^2$ G (nitrogen pressurization), sample oil temperature: 60°C, nozzle: Monarch 60° PL 2.25 (hollow cone type), distance between nozzle and burner: 10 cm, preliminary combustion time: 10 seconds, autoclave capacity: 1 L.

(9) Biodegradability test

**[0044]** Percent biodegradation is determined according to the modified MITI test method "OECD 301C." According to the Eco-mark certification revised in July, 1998, percent biodegradation is required to be 60% or more.

(10) Biodegradability and toxicity test

**[0045]** The test is carried out according to JIS K 0102. Japanese killifish is employed as a test fish, and 96-hour LC$_{50}$ is determined. According to the Eco-mark certification revised in July, 1998, 96-hour LC$_{50}$ is required to be 100 mg/L or more.

**[0046]** [Table 1]

Table 1

| | | | Example | | | | | | | Comparative Example | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 1 | 2 |
| (A) Base oil | TMP isostearic acid (oleic acid) partial ester | wt.% | 19.50 | 3.00 | 19.10 | 19.30 | 19.40 | 13.00 | 19.30 | 97.15 | - |
| | PE saturated fatty acid ester | wt.% | - | - | - | - | - | - | - | - | 31.50 |
| | TMP trioleate | wt.% | - | - | - | - | - | - | - | - | 66.25 |
| | High oleic rapeseed oil | wt.% | 77.45 | 92.95 | 75.85 | 76.65 | 77.05 | 83.45 | 77.05 | - | - |
| (B) PMA | PMA (1) | wt.% | 1.00 | 2.00 | 3.00 | - | 1.00 | - | 2.00 | 1.20 | 0.50 |
| | PMA (2) | wt.% | - | - | - | 2.00 | - | - | - | - | - |
| | PMA (3) | wt.% | - | - | - | - | 0.50 | - | - | - | - |
| | PMA (4) | wt.% | - | - | - | - | - | 1.50 | - | - | - |
| Additional additives | Phenyl α-naphthylamine | wt.% | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| | Ca sulfonate (TBN = 28) | wt.% | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| | 1,2,3-Benzotriazole | wt.% | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| | Pour-point-improving agent | wt.% | 0.30 | 0.30 | 0.30 | 0.30 | 0.30 | 0.30 | - | - | - |
| | Silicone antifoaming agent (product of Shin-Etsu Chemical Co., Ltd.) | wt.% | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | - | - | 0.10 |
| Total | | | 100.00 | 100.00 | 100.00 | 100.00 | 1.00.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| | | | | | | | | | | | |
| General Properties | Kinematic viscosity (40°C) | $mm^2/s$ | 45.56 | 46.11 | 54.01 | 46.88 | 47.60 | 42.04 | 50.08 | 68.91 | 44.77 |
| | Kinematic viscosity (100°C) | $mm^2/s$ | 9.536 | 10.050 | 11.300 | 9.748 | 9.953 | 9.224 | 10.450 | 11.520 | 8.675 |
| | index | - | 200 | 213 | 209 | 200 | 202 | 210 | 204 | 162 | 176 |
| | Viscosity Acid value | mg KOH/g | 0.15 | 0.11 | 0.13 | 0.12 | 0.11 | 0.12 | 0.15 | 0.32 | 0.67 |
| | Flash point | °C | 314 | 314 | 314 | 310 | 318 | 320 | 296 | 342 | 300 |

(continued)

| | | | Example | | | | | | | Comparative Example | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 1 | 2 |
| Lubricity | Corrosion resistance | - | 1 (1b) | 1 (1b) | 1 (1b) | 1 (1b) | 1 (1b) | 1 (1b) | 1 (1b) | 1 (1b) | 1 (1b) |
| | Rust prevention test | - | No rust | No rust | No rust | No rust | No rust | No rust | No rust | No rust | No rust |
| | Load bearing test (LWI) | N | 233 | 421 | 227 | 281 | 229 | 212 | 275 | 179 | 176 |
| Combustibility test | | sec | 2 > | 2 > | 5 | 8 | 4 | 3 | 2 | 4 | 30 < |
| Biodegradability test | | % | 85 | - | - | - | - | 85 | - | 65 | 77 |
| Biodegradability and toxicity test | | mg/L | 100 < | - | - | - | - | 100 < | - | 100 < | 100 < |

Industrial Applicability

**[0047]** The biodegradable lubricating oil composition of the present invention exhibits excellent flame retardancy and biodegradability. Therefore, the lubricating oil composition is suitable for use as, for example, a hydraulic oil employed as a power transmission fluid in a hydraulic system of, for example, a hydraulic machine or apparatus for power transmission, power control, power buffering, etc.; or a door closer oil employed for a door closer.

## Claims

**1.** A biodegradable lubricating oil composition comprising:

(A) a base oil containing (a) a plant-derived oil in an amount of 60 mass% or more, and (b) a polyol ester in an amount of 40 mass% or less; and
(B) a polymethacrylate having a mass average molecular weight of 20,000 to 300,000 in an amount of 0.1 to 5 mass%.

**2.** A biodegradable lubricating oil composition according to claim 1, wherein the plant-derived oil is rapeseed oil having an oleic acid content of 60 mass% or more.

**3.** A biodegradable lubricating oil composition according to claim 1 or 2, wherein the polyol ester is a polyol partial ester having a hydroxyl value of 30 mg KOH/g or more and a flash point of 300°C or higher.

**4.** A biodegradable lubricating oil composition according to any one of claims 1 to 3, which exhibits a kinematic viscosity at 40°C of 120 $mm^2/s$ or less.

**5.** A biodegradable lubricating oil composition according to any one of 1 to 4, which is employed as a hydraulic oil, a door closer oil, or a sliding surface oil.

**6.** A hydraulic oil comprising a biodegradable lubricating oil composition as recited in any one of claims 1 to 4.

**7.** A door closer oil comprising a biodegradable lubricating oil composition as recited in any one of claims 1 to 4.

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/057904

A. CLASSIFICATION OF SUBJECT MATTER
*C10M169/04*(2006.01)i, *C10M101/04*(2006.01)i, *C10M105/40*(2006.01)i, *C10M145/14*(2006.01)i, *C10N20/00*(2006.01)n, *C10N20/02*(2006.01)n, *C10N20/04*(2006.01)n, *C10N30/00*(2006.01)n, *C10N40/02*(2006.01)n, *C10N40/08*(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, C10M101/04, C10M105/40, C10M145/14, C10N20/00, C10N20/02, C10N20/04, C10N30/00, C10N40/02, C10N40/08

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 | 1996-2011 |
| Kokai Jitsuyo Shinan Koho | 1971-2011 | Toroku Jitsuyo Shinan Koho | 1994-2011 |

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 | WO 2008/134179 A2 (DOW GLOBAL TECHNOLOGIES INC.),<br>06 November 2008 (06.11.2008),<br>claims 1 to 14; page 1, lines 11 to 27; page 4, lines 20 to 28; tables 1 to 15; examples 1 to 51<br>& JP 2010-525150 A & US 2010/0120639 A1<br>& EP 2142624 A | 1-7 |
| Y | JP 2009-96995 A (Showa Shell Sekiyu Kabushiki Kaisha),<br>07 May 2009 (07.05.2009),<br>claim 1; paragraphs [0025], [0030]<br>& EP 2193186 A & WO 2009/040658 A1 | 1-7 |

☒ 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 | "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 |
| "E" earlier application or patent but published on or after the international filing date | "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 |
| "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) | "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 |
| "O" document referring to an oral disclosure, use, exhibition or other means | "&" document member of the same patent family |
| "P" document published prior to the international filing date but later than the priority date claimed | |

| | |
|---|---|
| Date of the actual completion of the international search<br>21 April, 2011 (21.04.11) | Date of mailing of the international search report<br>10 May, 2011 (10.05.11) |
| Name and mailing address of the ISA/<br>Japanese Patent Office<br>Facsimile No. | Authorized officer<br>Telephone No. |

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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2011/057904

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 2009-292997 A (Idemitsu Kosan Co., Ltd.),<br>17 December 2009 (17.12.2009),<br>claim 8; paragraph [0017]<br>(Family: none) | 1-7 |
| Y | WO 2009/032604 A1 (CHEVRON U.S.A. INC.),<br>12 March 2009 (12.03.2009),<br>page 18, line 23 to page 19, line 7<br>& JP 2008-531753 A & US 2007/0293408 A1 | 1-7 |
| Y | JP 6-228579 A (Idemitsu Kosan Co., Ltd.),<br>16 August 1994 (16.08.1994),<br>claims 1 to 6; paragraph [0008]; examples 1 to 19<br>& US 6402983 B1 & EP 612832 A1 | 3 |
| A | JP 11-269480 A (Idemitsu Kosan Co., Ltd.),<br>05 October 1999 (05.10.1999),<br>claims 1 to 4; examples 1, 2<br>(Family: none) | 1-7 |

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- JP 2558496 B **[0003]**
- JP 2888742 B **[0003]**
- JP H11269480 B **[0003]**
- JP 3017803 B **[0003]**