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(54) BIODEGRADABLE LUBRICATING OIL COMPOSITION

(57) The present invention provides a biodegradable lubricating oil composition containing 50% by mass or more of a synthetic ester base oil (A), 0.1 to 3% by mass of an amine-based antioxidant (B1), 0.1 to 3% by mass of a phenol-based antioxidant (B2), and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C), wherein the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more.

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Description

Technical Field

[0001] The present invention relates to a biodegradable lubricating oil composition containing a synthetic ester base oil.

Background Art

[0002] Recently, from the aspect of environmental pollution control measures, a biodegradable lubricating oil has been being put into practical use also in the field of lubricating oil. A biodegradable lubricating oil is required to have a high biodegradation rate, and, therefore, use of a large quantity of a mineral oil that is popularly used as a base oil in an ordinary lubricating oil is difficult. Consequently, the base oil must be selected from a limited range of a natural vegetable oil, a synthetic polyalkylene glycol base oil, a synthetic ester base oil and the like. Heretofore, among these, a synthetic ester base oil that is relatively excellent in heat stability and oxidation stability is much used.

[0003] As the synthetic ester base oil for use in a biodegradable lubricating oil, there are known fatty acid diesters in which an aliphatic dicarboxylic acid is used as the carboxylic acid, hindered esters in which an aliphatic hindered polyol is used as the polyol, etc. In addition, for example, PTL 1 discloses a biodegradable lubricating oil prepared by blending a phenol-based antioxidant, a low base number calcium sulfonate and a triazole compound in a base oil containing a hindered ester in an amount of 50% by mass or more for enhancing lubrication performance, oxidation stability and anticorrosion performance.

Citation List

Patent Literature

[0004] PTL 1:JP 2005-213451 A

Summary of Invention

Technical Problem

[0005] Performance of lubricating oil compositions is being desired to improve more year by year, and biodegradable lubricating oil compositions also have become required to have further prolonged lifetime and improved wear resistance. However, for example, as described in PTL 1, even though a hindered ester is used as a base oil and different kinds of additives are blended therein, it is still difficult to sufficient improve oxidation stability for lifetime prolongation, and in addition, wear resistance could not be improved sufficiently and the performance requirements could not be satisfied.

[0006] The present invention has been made in consideration of the above-mentioned problems and an object thereof is to provide a biodegradable lubricating oil composition having better wear resistance and enhanced oxidation stability.

Solution to Problem

[0007] As a result of assiduous studies, the present inventors have found that, when a specific synthetic ester base oil is used as a base oil and when the transmittance at 3,005 $\pm$ 1 cm^{-1} of the lubricating oil composition is made high, the resultant lubricating oil composition added with small quantities of additives added thereto can have sufficiently improved oxidation stability and wear resistance while maintaining good biodegradability, and have completed the present invention as described below. Specifically, the present invention provides the following:

(1) A biodegradable lubricating oil composition containing 50% by mass or more of a synthetic ester base oil (A), 0.1 to 3% by mass of an amine-based antioxidant (B1), 0.1 to 3% by mass of a phenol-based antioxidant (B2), and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C), wherein:

the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more.

(2) A method for producing a biodegradable lubricating oil composition, including blending at least 0.1 to 3% by mass of an amine-based antioxidant (B1), 0.1 to 3% by mass of a phenol-based antioxidant (B2) and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C) in 50% by mass or more of a synthetic ester base oil (A) to produce a biodegradable lubricating oil composition wherein the transmittance at 3,005 $\pm$ 1 cm^{-1} of

a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more.

Advantageous Effects of Invention

[0008] According to the present invention, there can be provided a biodegradable lubricating oil composition having good wear resistance and having enhanced oxidation stability.

Description of Embodiments

[0009] Hereinafter the present invention is described with reference to embodiments thereof.

[Biodegradable Lubricating Oil Composition]

[0010] The biodegradable lubricating oil composition of one aspect of the present invention contains at least 50% by mass or more of a synthetic ester base oil (A), as antioxidants (B), 0.1 to 3% by mass of an amine-based antioxidant (B1) and 0.1 to 3% by mass of a phenol-based antioxidant (B2), and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C).

[0011] Further, in the biodegradable lubricating oil composition of one aspect of the present invention, the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more. The transmittance at 3,005 $\pm$ 1 cm^{-1} in IR absorptiometry is an index of the amount of the unsaturated bonds in the biodegradable lubricating oil composition, and when the transmittance is 50% or more, the amount of the unsaturated bonds in the composition is small.

[0012] In the lubricating oil composition containing a synthetic ester base oil (A) as the main ingredient (in an amount of 50% by mass or more), as in this aspect, most of the unsaturated bonds are derived from the synthetic ester base oil (A), and in this, by reducing the amount of the unsaturated bonds in the synthetic ester base oil (A), the transmittance of the composition can be 50% or more. In this aspect, a synthetic ester base oil (A) having a small amount of unsaturated bonds therein is used to thereby reduce the amount of the unsaturated bonds in the lubricating oil composition, and consequently, by adding small quantities of the specific antioxidants (B) and the extreme-pressure agent (C), the oxidation stability and the wear resistance of the resultant biodegradable lubricating oil composition can be sufficiently improved.

[0013] The transmittance of the lubricating oil composition is, from the viewpoint of more reducing the amount of the unsaturated bonds in the lubricating oil composition, preferably 55% or more, and for making the composition contain few unsaturated bonds, the transmittance is more preferably 60% or more. The upper limit of the transmittance is 100%, but in view of the characteristics thereof, the transmittance is generally about 80% or less.

[0014] The components contained on the biodegradable lubricating oil composition are described in detail hereinunder.

[Synthetic Ester Base Oil (A)]

[0015] The synthetic ester base oil (A) may be adequately selected from ester bond-having synthetic base oils, and specifically may be selected from (A1) a polyol ester base oil being an ester of a polyol and an aliphatic monocarboxylic acid, (A2) a diester base oil being an ester of an aliphatic dicarboxylic acid and a monoalcohol, (A3) an ester base oil being a copolymer of an unsaturated dibasic acid ester and an α-olefin, etc. The synthetic ester base oil (A) may be one kind of an ester alone or may also be a mixture of two or more kinds of esters.

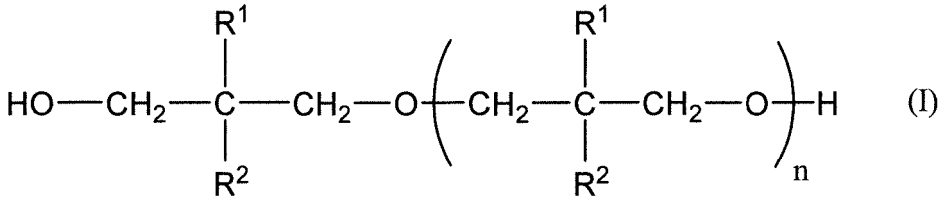
[0016] The synthetic ester base oil (A) for use in the lubricating oil composition is, for reducing the amount of the unsaturated bonds therein to thereby increase the transmittance of the lubricating oil composition as above, preferably so selected that the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, could be 50% or more, more preferably 55% or more, and even more preferably 60% or more so that the composition may contain few unsaturated bonds. The upper limit of the transmittance of the synthetic ester base oil (A) is 100%, but in view of the characteristics of the synthetic ester base oil (A), the transmittance thereof is generally about 80% or less.

[0017] For example, in the case where two or more kinds of synthetic ester base oils (A) are used in combination, preferably, two or more kinds of thereof having a transmittance of 50% or more are mixed. One having a transmittance of 50% or more and another having a transmittance of less than 50% may be mixed and used, but in the case, the lubricating oil composition preferably contains a larger amount of the one having a transmittance of 50% or more than the another having a transmittance of less than 50%.

[0018] The synthetic ester base oil (A) is contained in an amount of 50% by mass or more based on the total amount of the lubricating oil composition as above, but is preferably contained in an amount of 70% by mass or more, more preferably in an amount of 80% by mass or more, even more preferably in an amount of 90% by mass or more. The content of the synthetic ester base oil (A) relative to the total amount of the lubricating oil composition is less than 99.8%

by mass, but in order that the additives thereto to be mentioned below could be each in an adequate amount, the base oil content is preferably 99% by mass or less, more preferably 98% by mass or less.

[0019] The polyol ester base oil (A1) to be used as the synthetic ester base oil (A) includes a hindered ester, that is, an ester of a hindered polyol having one or more of quaternary carbons in the molecule where 1 to 4 methylol groups bond to at least one of the quaternary carbons, and an aliphatic monocarboxylic acid. More detailed examples of the hindered polyol include those having the following general formula (I):



(I)

wherein R^1 and R^2 each independently represent a hydrocarbon group having 1 to 6 carbon atoms, or a methylol group, and n represents an integer of 0 to 4.

[0020] In the above general formula (I), the hydrocarbon group having 1 to 6 carbon atoms of R^1 and R^2 is preferably a linear chain or branched chain alkyl group, more preferably an alkyl group having 1 or 2 carbon atoms. n is preferably an integer of 0 to 2.

[0021] Examples of the hindered polyol represented by the general formula (I) include a hindered polyol such as a dialkylpropanediol (where the alkyl group has 1 to 6 carbon atoms), a trimethylolalkane (where the alkane has 2 to 7 carbon atoms), a pentaerythritol, etc., and a dehydrated condensate thereof, and specifically include neopentyl glycol, 2-ethyl-2-methyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, trimethylolethane, trimethylolpropane, trimethylolbutane, trimethylolpentane, trimethylolhexane, trimethylolheptane, pentaerythritol, 2,2,6,6-tetramethyl-4-oxa-1,7-heptanediol, 2,2,6,6,10,10-hexamethyl-4,8-dioxa-1,11-undecadiol, 2,2,6,6,10,10,14,14-octamethyl-4,8,12-trioxa-1,15-pentadecadiol, 2,6-di(hydroxyethyl)-2,6-dimethyl-4-oxa-1,7-heptanediol, 2,6,10-tri(hydroxymethyl)-2,6,10-trimethyl-4,8-dioxa-1,11-undecadiol, 2,6,10,14-tetra(hydroxymethyl)-2,6,10,14-tetramethyl-4,8,12-trioxa-1,15-pentadec adiol, di(pentaerythritol), tri(pentaerythritol), tetra(pentaerythritol), penta(pentaerythritol), etc.

[0022] Among these hindered polyols, trimethylolpropane, neopentyl glycol, pentaerythritol, and bimolecular or trimolecular dehydrated condensates thereof are preferred; and above all, neopentyl glycol, trimethylolpropane and pentaerythritol are more preferred.

[0023] The aliphatic monocarboxylic acid to be used for the polyol ester base oil (A1) includes a saturated aliphatic monocarboxylic acid having 5 to 22 carbon atoms. The acyl group on the saturated aliphatic monocarboxylic acid may be linear or branched. Examples of the saturated aliphatic monocarboxylic acid of the type include a linear saturated monocarboxylic acid such as valeric acid, 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, behenic acid, etc.; a branched saturated monocarboxylic acid such as isomyristic acid, isopalmitic acid, isostearic acid, 2,2-dimethylpropanoic 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, 3,5,5-trimethylhexanoic acid, etc.

[0024] In esterification, one of these aliphatic monocarboxylic acids may be used singly or two or more kinds thereof may be used in combination. The polyol ester is generally a complete ester where all the hydroxyl groups in a polyol are esterified, but within a range not having any negative influence on the advantageous effects of the present invention, the polyol ester for use herein may contain a small amount of an ester where a part of hydroxyl groups are not esterified and remain as such.

[0025] As the diester base oil (A2), for example, an ester of a saturated dicarboxylic acid having 6 to 12 carbon atoms and an alkyl monoalcohol having 6 to 12 carbon atoms may be used. Examples of the saturated dicarboxylic acid include adipic acid, pimellic acid, suberic acid, azelaic acid, sebacic acid, undecane-diacid, dodecane-diacid, etc. Examples of the alkyl monoalcohol include a branched alkyl monoalcohol such as isooctanol, isononanol, isodecanol, 2-ethylhexanole, etc.; a linear alkyl monoalcohol such as n-octanol, n-nonanol, n-decanol, n-undecanol, n-dodecanol, etc. Preferred examples of the compounds include dioctyl adipate, diisononyl adipate, diisodecyl adipate, di-2-ethylhexyl azelate, diisooctyl azelate, diisononyl azelate, di-2-ethylhexyl sebacate, diisooctyl sebacate, diisononyl sebacate, di-2-ethylhexyl dodecanedioate, etc.

[0026] The ester to be used as the diester base oil (A2) may be an ester of one kind of alkylmonoalcohol and a saturated dicarboxylic acid, or may also be an ester of two kinds of alkylmonoalcohol and a saturated dicarboxylic acid.

[0027] Specifically, the ester base oil (A3) is a copolymer prepared by copolymerizing an ester of an unsaturated

dibasic acid and a monoalcohol, and an α-olefin. The unsaturated dibasic acid to be used here includes maleic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, etc. The monoalcohol includes an alkyl monoalcohol having 1 to 20 carbon atoms. Among these, an alkyl monoalcohol having 3 to 8 carbon atoms is more preferably used. The alkyl group of the alkyl monoalcohol may be linear or branched. Specifically, the alkyl monoalcohol includes methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, etc.

[0028] The α-olefin is preferably one having 3 to 20 carbon atoms, more preferably 6 to 18 carbon atoms. Examples of the α-olefin of the type include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, etc.

[0029] Preferably, the ester base oil (A3) has a kinematic viscosity at 100°C of 20 to 55 mm^2/s, more preferably 25 to 45 mm^2/s.

[0030] The above-mentioned various esters for use in the component (A) are generally produced by reacting a carboxylic acid and an alcohol, and, as a result, may have an ester structure formed of the above-mentioned carboxylic acid residue and the alcohol residue. Accordingly, it is not necessary to produce the component (A) by dehydration reaction of raw materials of the above-mentioned carboxylic acid and the alcohol, and the component may be produced according to any other method using other raw materials. For example, it may be produced according to an transesterification method.

[0031] Preferably, the synthetic ester base oil (A) contains the polyol ester base oil (A1) as the main ingredient among the above-mentioned synthetic ester base oils. Namely, the synthetic ester base oil (A) preferably contains the polyol ester base oil (A1) in an amount of more than 50% by mass relative to the total amount of the synthetic ester base oil (A), more preferably in an amount of 70 to 100% by mass, even more preferably 85 to 100% by mass.

[0032] Also preferably, the synthetic ester base oil (A) contains a polyol ester base oil (A1-1) having a total carbon number of 23 to 50 in one molecule as the main ingredient among the above-mentioned polyol ester base oil (A1) for the reason of kinematic viscosity, etc. Namely, the synthetic ester base oil (A) preferably contains a polyol ester base oil (A1-1) having a total carbon number of 23 to 50 in an amount of more than 50% by mass relative to the total amount of the synthetic ester base oil (A), more preferably in an amount of 70 to 100% by mass, even more preferably 75 to 100% by mass.

[0033] In the case where the synthetic ester base oil (A) contains a polyol ester base oil (A1-1) having a total carbon number of 23 to 50 as the main ingredient as mentioned above, the base oil (A) may further contain an ester base oil (A1-2) having a larger total carbon number in one molecule than that of the component (A1-1) among the above-mentioned polyol ester base oil (A1), and an ester base oil (A3) of the above-mentioned copolymer as the side ingredients. Here, specifically, the ester base oil (A1-2) having a larger total carbon number in one molecule than that of the component (A1-1) includes a polyol ester base oil (A1-2) having a total carbon number of 51 to 80 in one molecule.

[0034] The synthetic ester base oil (A) preferably contains at least one kind of ester selected from the polyol ester base oil (A1-2) having a total carbon number of 51 to 80 in one molecule, and the ester base oil (A3) of the above-mentioned copolymer, in a ratio of less than 50% by mass relative to the total amount of the ester base oil (A), more preferably in a ratio of 1 to 30% by mass, even more preferably 3 to 25% by mass.

[0035] Containing these (A1-2) and (A3) components as the side ingredients, the biodegradable lubricating oil composition may be readily controlled to have an adequate viscosity without losing oxidation stability and wear resistance.

[0036] For the polyol ester base oil (A1-1) having a total carbon number of 23 to 50, one or more is adequately selected from the above-exemplified ester base oil (A1), and preferred examples thereof include an ester of neopentyl glycol (having 6 carbon atoms) with a saturated aliphatic monocarboxylic acid having 9 to 22 carbon atoms, such as pelargonic acid, capric acid, undecanoic acid, lauryl acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, arachic acid, behenic acid, isomyristic acid, isopalmitic acid, isostearic 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, 3,5,5-trimethylhexanoic acid, etc.; an ester of pentaerythritol (having 5 carbon atoms) with a saturated aliphatic monocarboxylic acid having 5 to 11 carbon atoms, such as valeric acid, caproic acid, enanthic acid, caprylic acid (octanoic acid), pelargonic acid, capric acid (decanoic acid), undecanoic acid, 2,2-dimethylpropanoic 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, 2,3,3-trimethyl-2-ethylbutanoic acid, 2,3-dimethyl-2-isopropylbutanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid, etc.; and an ester of trimethylolpropane (having 6 carbon atoms) with a saturated aliphatic monocarboxylic acid having 6 to 14 carbon atoms, such as caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic 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, 3,5,5-trimethylhexanoic acid, etc.

[0037] As the component (A1-1) among these, an ester of pentaerythritol is preferred from the viewpoint of enhancing oxidation stability.

[0038] On the other hand, from the viewpoint of easiness in adequately controlling the viscosity without using the

above-mentioned component (A1-2) and the component (A3), the component (A1-1) is preferably an ester of neopentyl glycol. The carboxylic acid in the ester of neopentyl glycol is preferably a branched carboxylic acid, and more preferably a saturated aliphatic monocarboxylic acid having 16 to 20 carbon atoms.

[0039] Further, among the above-mentioned polyol ester base oil (A1-1), a polyol ester base oil having a total carbon number of 37 to 45 in one molecule is preferred.

[0040] As the polyol ester base oil (A1-2) having a total carbon number of 51 to 80, one or more may be selected from the polyol ester base oil (A1) that is an ester of a polyol and an aliphatic monocarboxylic acid as described above, and preferred examples thereof include an ester of pentaerythritol with a saturated higher aliphatic monocarboxylic acid having 12 to 18 carbon atoms, such as lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, isomyristic acid, isopalmitic acid, isostearic acid, 2,5,5-trimethyl-2-t-butylhexanoic acid, etc.; an ester of trimethylolpropane with a saturated higher aliphatic monocarboxylic acid having 15 to 22 carbon atoms, such as pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, arachic acid, behenic acid, isopalmitic acid, isostearic acid, etc.

[0041] As the component (A1-2), use of an ester of trimethylolpropane among these is preferred. Further, using an ester of pentaerythritol as the component (A1-1) is preferred along with using an ester of trimethylolpropane as the component (A1-2). Using such a mixed ester can adequately control the viscosity characteristics of the lubricating oil composition without detracting from various characteristics of the composition.

[0042] The total carbon number in one molecule of the polyol ester base oil (A1-2) is preferably 51 to 70.

[0043] In order to make the synthetic polyester base oil (A) have a transmittance of 50% or more, the ester may be controlled to contain few unsaturated bonds therein, and for example, as the component (A1), use of an ester of a specific polyol and a saturated aliphatic monocarboxylic acid as mentioned above can attain the intended purpose. Here, many commercial products are available for a saturated aliphatic monocarboxylic acid and an ester of the carboxylic acid, and such carboxylic acids or esters thereof may be adequately selected and used here. However, some commercial products of saturated aliphatic monocarboxylic acids or esters thereof may contain unsaturated bonds, and the esters could not have a transmittance of 50% or more. This is because saturated aliphatic monocarboxylic acids are generally produced from animal oil and vegetable oil containing a large quantity of unsaturated bonds.

[0044] On the other hand, the unsaturated bonds contained in animal oil and vegetable oil are generally hydrogenated and saturated during the production process, or are generally removed by purification. Consequently, in the component (A1) in this aspect, the saturated aliphatic monocarboxylic acid to be used as the raw material is preferably one having a high hydrogenation degree or one having a high purification degree to have a small quantity of unsaturated bonds.

[0045] Similarly, also in the components (A2) and (A3), the raw materials of alkyl monoalcohols and others are preferably ones having a high hydrogenation degree or having a high purification degree.

[0046] The base oil of the biodegradable lubricating oil composition may be the above-mentioned synthetic ester base oil (A) alone, but may contain any other base oil component than the above-mentioned synthetic ester base oil (A) within a range not detracting from the advantageous effects of the present invention. Specifically, the base oil may contain at least one selected from a polyether base oil such as a polyalkylene glycol, a polyvinyl ether, etc.; a mineral oil as exemplified by a paraffinic mineral oil, a napthenic mineral oil, an intermediate base mineral oil, etc.; a synthetic hydrocarbon oil such as a polybutene, a polypropylene, an olefin copolymer, etc. However, the content of the other base oil component than the synthetic ester base oil (A) is preferably less than 20% by mass based on the total amount of the lubricating oil composition in order that the composition may secure high biodegradability as described below, more preferably less than 10% by mass.

[Antioxidant (B)]

[0047] The biodegradable lubricating oil composition of this aspect contains, as antioxidants (B), both of an amine-based antioxidant (B1) and a phenol-based antioxidant (B2). In this aspect, these two antioxidants are blended in the above-mentioned specific synthetic ester base oil (A), and therefore though the amount of each component to be blended is small, the resultant composition can exhibit high oxidation stability.

[0048] The amine-based antioxidant (B1) includes a monoalkyldiphenylamine in which the alkyl group has 4 to 12 carbon atoms, such as mono-t-butyldiphenylamine, monooctyldiphenylamine, monononyldiphenylamine, etc.; a dialkyldiphenylamine in which the alkyl group each has 4 to 12 carbon atoms, such as 4,4'-dibutyldiphenylamine, 4,4'-dipentyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine, 4,4'-dinonyldiphenylamine, 4-butyl-4'-octyldiphenylamine, etc.; a polyalkyldiphenylamine in which the alkyl group each has 1 to 10 carbon atoms, such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, tetranonyldiphenylamine, di(2,4-diethylphenyl)amine, di(2-ethyl-4-nonylphenyl)amine, etc.; a polyalkyldiphenylamine which has 3 alkyl groups and in which the alkyl group each has 1 to 10 carbon atoms, such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, tetranonyldiphenylamine, di(2,4-diethylphenyl)amine, di(2-ethyl-4-nonylphenyl)amine, etc.; phenyl-α-naphthylamines as exemplified by an alkylphenyl-α-naphthylamine having at least one alkyl group having 1

to 12 carbon atoms, such as methylphenyl-α-naphthylamine, ethylphenyl-α-naphthylamine, butylphenyl-α-naphthylamine, hexylphenyl-α-naphthylamine, heptylphenyl-α-naphthylamine, Octylphenyl-α-naphthylamine, nonylphenyl-α-naphthylamine, t-dodecylphenyl-α-naphthylamine, etc., or phenyl-α-naphthylamine, etc.

[0049] As the amine-based antioxidant (B1), using a dialkyldiphenylamine or an alkylphenyl-α-naphthylamine among the above is preferred, and using a dialkyldiphenylamine is more preferred.

<Phenol-Based Antioxidant (B2)>

[0050] The phenol-based antioxidant (B2) includes a monophenol-based antioxidant and a bisphenol-based antioxidant.

[0051] The monophenol-based antioxidant includes an alkyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (in which the alkyl group includes one having 4 to 20 carbon atoms, preferably 8 to 18 carbon atoms) such as n-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 6-methylheptyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, etc.; a 2,6-di-t-butyl-4-alkylphenol (in which the alkyl group has 1 to 4 carbon atoms) such as 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, etc.; 2,4-dimethyl-6-t-butylphenol, 2,6-di-t-amyl-p-cresol, etc.

[0052] The bisphenol antioxidant includes 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 4,4'-bis(2-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 4,4'-isopropylidenebis(2,6-di-t-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 4,4'-thiobis(2-methyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), 2,2'-thiobis(4-methyl-6-t-butylphenol), bis(3-methyl-4-hydroxy-5-t-butylbenzyl) sulfide, bis(3,5-di-t-butyl-4-hydroxybenzyl) sulfide, thiodiethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], etc.

[0053] The phenol-based antioxidant is preferably a monophenol-based antioxidant among the above, and above all, an alkyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate is more preferred.

[0054] The biodegradable lubricating oil composition contains the amine-based antioxidant (B1) in an amount of 0.1 to 3% by mass and the phenol-based antioxidant (B2) in an amount of 0.1 to 3% by mass based on the total amount of the composition, as mentioned above. The content of these antioxidants (B1) and (B2) is controlled to be each 0.1% by mass or more so that the biodegradable lubricating oil composition can be given high oxidation stability. In addition, the content thereof is controlled to be each 3% by mass or less so that the biodegradable lubricating oil composition can exhibit the advantageous effects commensurate with the content and reduction in the biodegradability of the composition owing to the antioxidants (B) therein can be prevented. In particular, the amine-based antioxidant (B1) is often a factor of reducing the biodegradability of the lubricating oil composition, but in this aspect, the antioxidant is used along with the above-mentioned specific synthetic ester base oil (A), and therefore even a small amount of the amine-based antioxidant (B1) can sufficiently enhance the oxidation stability of the composition. Consequently, in this aspect, the reduction in the biodegradability can be minimized.

[0055] In addition, for more enhancing oxidation stability while preventing reduction in biodegradability, the content of the amine-based antioxidant (B1) is preferably 0.2 to 2.5% by mass, more preferably 0.3 to 1.8% by mass. From the same viewpoint, the content of the phenol-based antioxidant (B2) is preferably 0.2 to 2.5% by mass, more preferably 0.3 to 1.5% by mass.

[Sulfur-Phosphorus-Based Extreme-Pressure Agent (C)]

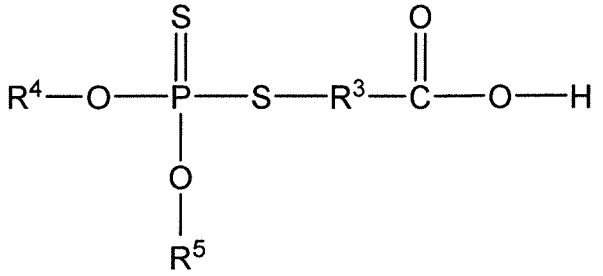
[0056] The biodegradable lubricating oil composition of this aspect further contains a sulfur-phosphorus-based extreme-pressure agent (C). When the composition contains the synthetic ester base oil (A) as above, the composition could not exhibit extreme-pressure performance even though an extreme-pressure agent is added thereto. However, among extreme-pressure agents, a sulfur-phosphorus-based extreme-pressure agent (C) is added thereto, and therefore the lubricating oil composition can sufficiently exhibit extreme-pressure performance and can better wear resistance thereof.

[0057] The sulfur-phosphorus-based extreme-pressure agent (C) to be used includes monothiophosphates, dithiophosphates, trithiophosphates, monothiophosphate amine salts, dithiophosphate amine salts, monothiophosphites, dithiophosphites, trithiophosphites, etc. Among these, dithiophosphates are preferred.

[0058] From the viewpoint of bettering wear resistance, dithiophosphates having a terminal carboxyl group are preferred among dithiophosphates. When having a terminal carboxyl group, the sulfur-phosphorus-based extreme-pressure agent (C) can have an increased polarity, and therefore in this aspect using the above-mentioned specific synthetic ester base oil (A) as the base oil, the sulfur-phosphorus-based extreme-pressure agent (C) can readily exhibit the function of an extreme-pressure agent.

[0059] Specific examples of the dithiophosphate having a terminal carboxyl group include compounds represented

by the following general formula (II):



(II)

wherein R^3 represents a linear or branched alkylene group having 1 to 8 carbon atoms, and R^4 and R^5 each independently represent a hydrocarbon group having 3 to 20 carbon atoms.

[0060] In the formula (II), R^3 is, from the viewpoint of bettering solubility in base oil, preferably a linear or branched alkylene group having 1 to 8 carbon atoms, more preferably a linear or branched alkylene group having 2 to 4 carbon atoms, and even more preferably a branched alkylene group. Specifically, $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2CH_3)-$, $CH_2CH(CH_3)CH_2-$ and $-CH_2CH(CH_2CH_2CH_3)-$are preferred; $-CH_2CH(CH_3)-$ and $-CH_2CH(CH_3)CH_2-$ are more preferred; and $-CH_2CH(CH_3)-$ is even more preferred.

[0061] R^4 and R^5 each are, from the viewpoint of bettering extreme-pressure performance and bettering solubility in base oil, preferably a linear or branched alkyl group having 3 to 8 carbon atoms, more preferably a linear or branched alkyl group having 4 to 6 carbon atoms. Specifically, the group is preferably selected from the group consisting propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, isopentyl, hexyl, 2-ethylbutyl, 1-methylpentyl, 1,3-dimethylbutyl and 2-ethylhexyl groups. Among these, isobutyl and t-butyl are more preferred.

[0062] The biodegradable lubricating oil composition contains the sulfur-phosphorus-based extreme-pressure agent (C) in an amount of 0.01 to 2% by mass based on the total amount of the composition, as mentioned above. When the content of the sulfur-phosphorus-based extreme-pressure agent (C) is 0.01% by mass or more, the lubricating oil composition can be given extreme-pressure property to better wear resistance thereof. When the content is 2% by mass or less, the composition can exhibit the effect commensurate with the content to thereby prevent the biodegradability and the oxidation stability of the biodegradable lubricating oil composition from being lowered owing to the sulfur-phosphorus-based extreme-pressure agent (C).

[0063] For more preventing biodegradability and oxidation stability from being lowered and for more enhancing wear resistance, the content of the sulfur-phosphorus-based extreme-pressure additive (C) is preferably 0.02 to 1% by mass, more preferably 0.03 to 0.5% by mass.

[Viscosity Index Improver]

[0064] The biodegradable lubricating oil composition of this aspect may contain a viscosity index improver.

[0065] The viscosity index improver includes a polymethacrylate, a dispersive polymethacrylate, an olefin copolymer (for example, an ethylene-propylene copolymer, etc.), a dispersive olefin copolymer, a styrene copolymer (for example, a styrene-diene copolymer, a styrene-isoprene copolymer, etc.), etc. Among these, a polymethacrylate is preferred. The polymethacrylate usable as a viscosity index improver generally has a weight-average molecular weight of 10,000 to 70,000, preferably 20,000 to 55,000. The weight-average molecular weight is a value measured through gel permeation chromatography and derived from a calibration curve drawn using polystyrene.

[0066] The content of the viscosity index improver is preferably 0.1 to 10% by mass based on the total amount of the lubricating oil composition, more preferably 0.5 to 5% by mass.

[Triazole Compound]

[0067] The biodegradable lubricating oil composition of this aspect may further contain a triazole compound. The triazole compound acts as a metal inactivator, and imparts an anticorrosive effect against non-ferrous metals to the biodegradable lubricating oil composition. Specific examples of the triazole compound include benzotriazole, carboxybenzotriazole, 3-aminotriazole, 4-aminotriazole, 2,5-diaminotriazole, 3-mercaptotriazole, and N-dialkyl (with 3 to 12 carbon atoms)aminomethyl-1,2,3-benzotriazole such as N-diethylaminomethyl-1,2,3-benzotriazole, etc. Those having a benzotriazole skeleton (benzotriazole compounds) are preferred.

[0068] The content of the triazole compound is preferably 0.01 to 1% by mass based on the total amount of the lubricating oil composition, more preferably 0.02 to 0.5% by mass.

[Rust Inhibitor]

[0069] The biodegradable lubricating oil composition may contain at least one selected from an alkaline earth metal sulfonate and a succinate, as a rust inhibitor. Containing a rust inhibitor, the biodegradable lubricating oil composition can have an increased corrosion-resistant effect against metals such as iron, etc.

[0070] The alkaline earth metal sulfonate is one prepared by sulfonating an alkylaromatic compound followed by converting it into an alkaline earth metal salt thereof, and includes a calcium sulfonate, a magnesium sulfonate and a barium sulfonate. Among these, a calcium sulfonate is preferred. The alkaline earth metal sulfonate preferably has a low basicity, and specifically the total base number (TBN) thereof is preferably 0 to 100 mgKOH/g, more preferably 0 to 50 mgKOH/g. The total base number is measured according to a perchloric acid method of JIS K-2501. Using an alkaline earth metal sulfonate, the composition can additionally exhibit a detergent-dispersant effect.

[0071] The alkenyl succinate includes a half ester of an alkenylsuccinic acid with an alcohol such as a polyalcohol, etc.

[0072] One of the rust inhibitors may be used singly or two or more kinds thereof may be used in combination. The content of the rust inhibitor is preferably within a range of 0.01 to 1.0% by mass based on the total amount of the lubricating oil composition, more preferably 0.03 to 0.5% by mass.

(Other Additives)

[0073] The biodegradable lubricating oil composition may contain any other extreme-pressure additive than the sulfur-phosphorus-based extreme-pressure agent (C). Specifically, the other extreme-pressure agent includes a phosphorus-based extreme-pressure agent such as a phosphate, e.g., tricresyl phosphate (TCP), an acidic phosphate amine salt, a phosphite, etc. The content of the phosphorus-based extreme-pressure agent is preferably 0.1 to 2% by mass based on the total amount of the lubricating oil composition, more preferably 0.2 to 1.5% by mass.

[0074] The biodegradable lubricating oil composition may contain any other additive than the above, such as an ashless dispersant, a pour point depressant, an anti-foam agent, a surfactant, a demulsifier, etc.

[0075] Examples of the ashless dispersant include a succinimide, a boron-containing succinimide, a benzylamine, a boron-containing benzylamine, etc.

[0076] The pour point depressant includes an ethylene-vinyl acetate copolymer, a condensate of a chloroparaffin and a naphthalene, a condensate of a chloroparaffin and a phenol, a polymethacrylate, a polyalkylstyrene, etc. The anti-foam agent may be a silicone anti-foam agent or a non-silicone anti-foam agent.

[Property of Biodegradable Lubricating Oil Composition]

[0077] The biodegradable lubricating oil composition of this aspect preferably has a biodegradation rate of 60% or more as measured in a degradation test for chemical substances with microbes according to the 301B test of the OECD Test Guideline, more preferably 70% or more. In this aspect, the specific synthetic ester base oil (A) is used as the main component, and the amount of various additives of the antioxidants (B1) and (B2) and the sulfur-phosphorus-based extreme-pressure agent (C) is controlled to be a predetermined amount or less, and the biodegradation rate of the composition can be thereby increased.

[0078] The kinematic viscosity at 40°C of the biodegradable lubricating oil composition is preferably 10 to 150 mm^2/s, more preferably 15 to 100 mm^2/s. The viscosity index of the composition is preferably 130 or more, more preferably 135 or more. Having a kinematic viscosity and a viscosity index each falling within the range, the biodegradable lubricating oil composition can be adequately used as a lubricating oil in various uses to be mentioned hereinunder.

[0079] The biodegradable lubricating oil composition of this aspect can be favorably used, for example, for a hydraulic fluid that is a power transmission fluid for use for power transmission, power control, buffer or the like in a hydraulic system; a lubricating oil or a universal oil for transmissions of agricultural tractors, or construction or civil engineering machines; an oil for chain saws; a 2-cycle engine oil; an industrial gear oil for wind-power generation, etc. Among these, the composition is more preferably used as a hydraulic fluid.

[Production Method for Biodegradable Lubricating Oil Composition]

[0080] A production method for the biodegradable lubricating oil composition in this aspect includes blending at least 0.1 to 3% by mass of an amine-based antioxidant (B1), 0.1 to 3% by mass of a phenol-based antioxidant (B2) and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C) in 50% by mass or more of a synthetic ester base oil (A) to produce a biodegradable lubricating oil composition wherein the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more. As described above, any other components than these components (A), (B1), (B2) and (C) may be blended in the biodegradable lubricating oil composition.

[0081] The details of the components (A), (B1), (B2) and (C), and the other components than these and details of the obtained biodegradable lubricating oil composition are as described above, and are therefore omitted herein.

Examples

[0082] The present invention is described more specifically with reference to Examples, but the present invention is not whatsoever restricted by these Examples.

[0083] Various properties of the lubricating oil composition were measured and evaluated according to the methods mentioned below.

(1) Kinematic Viscosity (40°C, 100°C)

[0084] Measured according to JIS K 2283.

(2) Viscosity Index

[0085] Measured according to JIS K 2283.

(3) Acid Value

[0086] Measured in an indicator method according to JIS K 2501.

(4) IR Spectrometry

[0087] Using an IR spectrometer (trade name, FT-IR6200, manufactured by JASCO Corporation), a lubricating oil composition was introduced between potassium bromide cells via a 0.1 mm-thick spacer to form a 0.1 mm-thick liquid film therebetween, and the transmittance thereof at 4,000 to 400 cm^{-1} was measured at a resolution of 4 cm^{-1} for a number of 16 scans, and then the transmittance at 3,005 $\pm$ 1 cm^{-1} was read to be the transmittance of the lubricating oil composition.

[0088] In place of the lubricating oil composition, a synthetic ester base oil was introduced between the cells, and the transmittance of the synthetic ester base oil was measured according to the same method as above.

(5) Shell Wear Test

[0089] Using a shell wear tester and according to ASTM D 2783, the load bearing performance of the lubricating oil composition was evaluated under the test conditions of a load of 294 N, a rotating speed of 1,200 rpm, a temperature of 50°C, and for a test period of 30 minutes. The result was expressed as the wear track (mm) by the test steel ball.

[0090] In this test, when the wear track is 0.5 mm or less, the wear resistance is evaluated as good "A", but when the wear track is more than 0.5 mm, the wear resistance is evaluated as insufficient "B".

(6) RBOT Test

[0091] According to the rotating cylinder-type oxidation stability test of JIS K 2514-3, the lubricating oil composition was tested at a test temperature of 150°C and under a pressure of 620 kPa, and the time taken until the pressure lowered by 175 kPa from the maximum pressure was measured.

[0092] In this test, when the RBOT value is 250 minutes or more, the tested composition is evaluated as good "A" since its oxidation stability is sufficient in use, for example, as a compression hydraulic oil, but when the value is less than 250 minutes, the tested composition is evaluated as not good "B" since the oxidation stability thereof is insufficient.

(7) ISOT Test

[0093] According to JIS K 2514-1, a copper/iron catalyst was made to exist in a sample oil, and the sample oil was aged at a test temperature of 130°C for a test period of 168 hours. A value calculated by dividing the kinematic viscosity at 40°C of the aged oil by the kinematic viscosity at 40°C of the unaged oil was referred to as a viscosity ratio. In addition, the acid value of the aged oil was subtracted from the acid value of the unaged oil to give an acid value increase.

Examples 1 to 4, Comparative Examples 1 to 6

[0094] Biodegradable lubricating oil compositions were prepared in the blending formulation shown in Table 1, and tested to determine and evaluate the properties thereof. The results are shown in Table 1.

Table 1

		Transmittance	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Base Oil	PE Saturated Fatty Acid Ester	65%	85.20	75.90	85.30		31.60			31.55		81.50
	NPG Saturated Fatty Acid Ester	70%				97.72						
	TMP Saturated Higher Fatty Acid Ester	65%		19.25								
	Copolymer of Unsaturated Dibasic Acid Ester and α-Olefin	65%	10.55		10.45							16.70
	TMP Unsaturated Fatty Acid Ester	38%					66.20			66.20		
	TMP Saturated/Unsaturated Fatty Acid Ester	45%						70.33	69.78		71.13	
	TMP Saturated Lower Fatty Acid Ester	65%						27.35	27.12		27.63	
Additives	Amine-Based Antioxidant (B1)		0.40	1.50	0.40	0.40		1.50	1.50	1.20	0.35	0.40
	Phenol-Based Antioxidant (B2)		1.00	0.50	1.00	1.00	1.40			0.20	0.02	0.40
	Sulfur-Phosphorus-Based Extreme-Pressure Agent (C)		0.05	0.05	0.10	0.05						
	PMA (1)						0.50	0.50	0.50	0.50	0.50	0.50
	PMA (2)		2.00	2.00	2.00							
	Benzotriazole Compound		0.10	0.10	0.05	0.03	0.10	0.10	0.10	0.10	0.10	0.10
	Rust Inhibitor (1)		0.10	0.10		0.20	0.10	0.10	0.10	0.10	0.10	0.10
	Rust Inhibitor (2)				0.10							
	Phosphorus-Based Extreme-Pressure Agent (1)		0.50	0.50	0.50	0.50			0.80			0.20
	Phosphorus-Based Extreme-Pressure Agent (2)							0.02		0.05	0.07	0.10
	Anti-foam Agent		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	
Total			100	100	100	100	100	100	100	100	100	100
Transmittance of Total Amount of Composition			65%	65%	65%	70%	45%	48%	48%	45%	48%	65%
Properties Evaluation Results of Composition	Kinematic Viscosity (40°C)	mm^2/s	46.13	48.75	45.69	45.13	45.43	48.80	48.44	45.34	47.65	46.88
	Kinematic Viscosity (100°C)	mm^2/s	7.747	8.010	7.770	7.977	8.765	8.818	8.752	8.740	8.746	7.858
	Viscosity Index		137	135	139	150	176	162	161	176	165	137
	Acid Value (initial)	mgKOH/g	0.28	0.18	0.36	0.16	0.91	0.61	0.57	0.91	0.64	0.56
	Shell Wear (50°C, 294 N, 30 min)	mm	0.43	0.37	0.40	0.38	0.70	0.64	0.66	0.65	0.62	0.63
		Evaluation	A	A	A	A	B	B	B	B	B	B
	RBOT, 150°C, 620 kPa	min	671	1035	694	390	67	639	639	434	127	731
		Evaluation	A	A	A	A	B	A	A	A	B	A
	ISOT (130°C × 168 h)											
	Viscosity Ratio (40°C)	-	1.02	1.02	1.00	1.00	3.29	1.26	1.25	1.40	3.56	1.01
	Acid Value Increase	mgKOH/g	-0.02	0.09	0.16	0.05	14.69	0.96	0.93	2.17	7.18	-0.17

* The numeral values in the columns of base oil and additives are in terms of % by mass relative to the total amount of the lubricating oil composition.

[0095] The components in Table 1 are as follows.

(Base Oil)

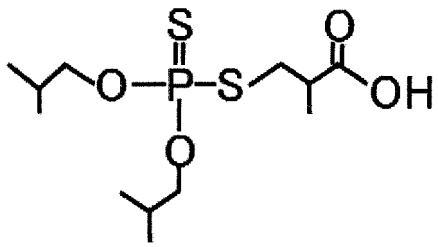
[0096]

PE saturated fatty acid ester: complete ester of pentaerythritol and a mixture of octanoic acid and decanoic acid (transmittance at 3,005 ± 1 cm^{-1}: 65%)
NPG saturated fatty acid ester: complete ester of neopentyl glycol and isostearic acid (transmittance at 3,005 ± 1 cm^{-1}: 70%)
TMP saturated higher fatty acid ester: complete ester of trimethylolpropane and isostearic acid (transmittance at 3,005 ± 1 cm^{-1}: 65%)
Copolymer of unsaturated dibasic ester and α-olefin: copolymer of maleic acid butanol ester and α-olefin having 6 to 18 carbon atoms (100°C kinematic viscosity: 35 mm^2/s, transmittance at 3,005 ± 1 cm^{-1}: 65%)
TMP unsaturated fatty acid ester: complete ester of trimethylolpropane and oleic acid (transmittance at 3,005 ± 1 cm^{-1}: 38%)
TMP saturated/unsaturated fatty acid ester: complete ester of trimethylolpropane and a mixture of isostearic acid and oleic acid (transmittance at 3,005 ± 1 cm^{-1}: 45%)
TMP saturated lower fatty acid ester: complete ester of trimethylolpropane and a mixture of caprylic acid and capric acid (transmittance at 3,005 ± 1 cm^{-1}: 65%)

(Additives)

[0097]

Amine-based antioxidant (B1): 4-butyl-4'-octyldiphenylamine
Phenol-based antioxidant (B2): n-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate
Sulfur-phosphorus-based extreme-pressure agent (C): compound represented by the following chemical formula:



PMA (1): polymethacrylate (weight-average molecular weight: 180,000)
PMA (2): polymethacrylate (weight-average molecular weight: 45,000) Benzotriazole compound: 1,2,3-benzotriazole
Rust inhibitor (1): low-basic calcium sulfonate (total base number 28 mgKOH/g)
Rust inhibitor (2): half ester of alkenylsuccinic acid and polyalcohol Phosphorus-based extreme-pressure agent (1): tricresyl phosphate (TCP) Phosphorus-based extreme-pressure agent (2): oleyl acid phosphate
Anti-foam agent: silicone anti-foam agent

[0098] As described above, in Examples 1 to 4, the synthetic ester base oil (A) having a high transmittance was used in order that the transmittance at 3,005 ± 1 cm^{-1} of the lubricating oil composition could be 50% or more, and the amine-based antioxidant (B1), the phenol-based antioxidant (B2) and the sulfur-phosphorus-based extreme-pressure agent (C) were contained each in a predetermined amount, and therefore, the RBOT value of the composition was sufficiently large and, in addition, the viscosity increase and the acid value increase in the ISOT test could be prevented from increasing, that is, the oxidation stability of the composition was good in various environments. Further, the wear loss in the Shell wear test was small, and the wear resistance of the composition was good.

[0099] As opposed to these, in Comparative Examples 1 to 3, the transmittance of the lubricating oil composition was less than 50%, and therefore in the ISOT test, the viscosity increased and the acid value increased, that is, the oxidation stability of the composition could not be sufficiently bettered. This tendency was also seen in Comparative Examples 4 and 5 where both the amine-based antioxidant (B1) and the phenol-based antioxidant (B2) were contained. In Comparative Example 6, though the oxidation stability was good, the wear resistance could not be enhanced since the composition did not contain the sulfur-phosphorus extreme-pressure agent (C).

Claims

1. A biodegradable lubricating oil composition comprising 50% by mass or more of a synthetic ester base oil (A), 0.1 to 3% by mass of an amine-based antioxidant (B1), 0.1 to 3% by mass of a phenol-based antioxidant (B2), and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C), wherein:

   the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more.

2. The biodegradable lubricating oil composition according to claim 1, wherein the synthetic ester base oil (A) comprises a polyol ester base oil (A1) being an ester of a polyol and an aliphatic monocarboxylic acid in an amount of more than 50% by mass relative to the total amount of the synthetic ester base oil (A).

3. The biodegradable lubricating oil composition according to claim 2, wherein the polyol ester base oil (A1) is an ester of a hindered polyol having one or more of quaternary carbons in the molecule and having 1 to 4 methylol groups bonding to at least one of the quaternary carbon atoms, and an aliphatic monocarboxylic acid.

4. The biodegradable lubricating oil composition according to any one of claims 1 to 3, wherein the synthetic ester base oil (A) comprises at least a polyol ester base oil (A1-1) being an ester of a polyol and an aliphatic monocarboxylic acid and having a total carbon number of 23 to 50 in one molecule in an amount of more than 50% by mass relative to the total amount of the synthetic ester base oil (A).

5. The biodegradable lubricating oil composition according to claim 4, wherein the polyol ester base oil (A1-1) is at least one base oil selected from an ester of a neopentyl glycol and a saturated aliphatic monocarboxylic acid having 9 to 22 carbon atoms, and an ester of a pentaerythritol and a saturated aliphatic monocarboxylic acid having 5 to 11 carbon atoms.

6. The biodegradable lubricating oil composition according to claim 4 or 5, wherein the synthetic ester base oil (A) further comprises at least one base oil selected from a polyol ester base oil (A1-2) being an ester of a polyol and an aliphatic monocarboxylic acid and having a total carbon number of 51 to 80 in one molecule and a copolymer (A3) of an unsaturated dibasic acid ester and an α-olefin in an amount of less than 50% by mass relative to the total amount of the synthetic ester base oil (A).

7. The biodegradable lubricating oil composition according to claim 6, wherein the polyol ester base oil (A1-2) is an ester of a trimethylolpropane and a saturated higher aliphatic monocarboxylic acid having 15 to 22 carbon atoms.

8. The biodegradable lubricating oil composition according to any one of claims 1 to 7, wherein the sulfur-phosphorus-based extreme-pressure agent is a dithiophosphate having a terminal carboxyl group.

9. The biodegradable lubricating oil composition according to any one of claims 1 to 8, wherein the amine-based antioxidant (B1) is a dialkyldiphenylamine.

10. The biodegradable lubricating oil composition according to any one of claims 1 to 9, wherein the phenol-based antioxidant (B2) is an alkyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate.

11. The biodegradable lubricating oil composition according to any one of claims 1 to 10, further comprising a viscosity index improver in an amount of 0.1 to 10% by mass.

12. The biodegradable lubricating oil composition according to any one of claims 1 to 11, further comprising a triazole compound in an amount of 0.01 to 1 % by mass.

13. The biodegradable lubricating oil composition according to any one of claims 1 to 12, which has a biodegradation rate of 60% or more as measured in a degradation test for chemical substances with microbes according to the 301B test of the OECD Test Guideline.

14. The biodegradable lubricating oil composition according to any one of claims 1 to 13, which is for a hydraulic fluid.

15. A method for producing a biodegradable lubricating oil composition, comprising blending at least 0.1 to 3% by mass

of an amine-based antioxidant (B1), 0.1 to 3% by mass of a phenol-based antioxidant (B2) and 0.01 to 2% by mass of a sulfur-phosphorus-based extreme-pressure agent (C) in 50% by mass or more of a synthetic ester base oil (A) to produce a biodegradable lubricating oil composition wherein the transmittance at 3,005 $\pm$ 1 cm^{-1} of a 0.1 mm-thick liquid film of the composition, as measured through IR absorptiometry, is 50% or more.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/055590

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M169/04, C10M105/32, C10M105/38, C10M129/10, C10M129/76, C10M133/12, C10M137/10, C10N20/00, C10N30/00, C10N40/04, C10N40/06, C10N40/08, C10N40/26, C10N40/32

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 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Japio-GPG/FX & keyword: lubrication, biodegradation, ester, base oil and related terms,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2010-265397 A (Idemitsu Kosan Co., Ltd.), 25 November 2010 (25.11.2010), claims; paragraphs [0001] to [0067]; examples 1 to 2; comparative examples 1 to 2 & US 2012/0065111 A1 claims; paragraphs [0001] to [0128] & WO 2010/131739 A1 & EP 002431450 A1 & CN 102421882 A & DK 002431450 T	1-5,9-15 4-8
X Y	JP 2014-095088 A (Idemitsu Kosan Co., Ltd.), 22 May 2014 (22.05.2014), claims; paragraphs [0001] to [0067]; examples 1 to 2; comparative examples 1 to 2 & JP 2010-265397 A	1-5,9-15 4-8

☒ 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
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"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
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 April 2016 (27.04.16)	17 May 2016 (17.05.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2013-053227 A (Idemitsu Kosan Co., Ltd.), 21 March 2013 (21.03.2013), claims; paragraphs [0001] to [0053]; examples & US 2014/0296117 A1 claims; paragraphs [0001] to [0107] & WO 2013/031894 A1 & EP 002752480 A1 & CN 103781888 A	1-5,9-15 4-8
Y	WO 2011/086800 A1 (JX Nippon Oil & Energy Corp.), 21 July 2011 (21.07.2011), claims; paragraphs [0050], [0162] & US 2012/0322706 A1 claims; paragraphs [0064], [0197] & JP 2011-162766 A & EP 002527420 A1 & CN 102712871 A & KR 10-2012-0125271 A	4-7
Y	JP 2000-160177 A (Idemitsu Kosan Co., Ltd.), 13 June 2000 (13.06.2000), claims; paragraphs [0001] to [0011], [0022]; examples (Family: none)	6-7
Y	JP 2014-208853 A (JX Nippon Oil & Energy Corp.), 06 November 2014 (06.11.2014), claims; paragraphs [0162] to [0163] (Family: none)	8
P,X	JP 2015-147859 A (Cosmo Oil Lubricants Co., Ltd.), 20 August 2015 (20.08.2015), claims; paragraphs [0001] to [0093]; examples (Family: none)	1-4,8-15
A	JP 2011-137089 A (Lion Corp.), 14 July 2011 (14.07.2011), claims; paragraphs [0001] to [0018] (Family: none)	1-15
A	JP 2004-527592 A (Hatco Corp.), 09 September 2004 (09.09.2004), claims; paragraphs [0001] to [0058] & US 2002/0193260 A1 claims; paragraphs [0001] to [0064] & WO 2002/053688 A2 & EP 1356013 A2 & DE 60232640 D & CA 2433575 A & IL 156747 D & NZ 526838 A & AT 434028 T & HK 1063060 A & KR 10-0814149 B1 & IL 156747 A & AU 2002234196 B	1-15

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/055590

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-161664 A (Nippon Oil Corp.), 23 July 2009 (23.07.2009), claims; paragraphs [0001] to [0094] (Family: none)	1-15

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INTERNATIONAL SEARCH REPORT

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PCT/JP2016/055590

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

C10M169/04(2006.01)i, *C10M105/32*(2006.01)n, *C10M105/38*(2006.01)n, *C10M129/10*(2006.01)n, *C10M129/76*(2006.01)n, *C10M133/12*(2006.01)n, *C10M137/10*(2006.01)n, *C10N20/00*(2006.01)n, *C10N30/00*(2006.01)n, *C10N40/04*(2006.01)n, *C10N40/06*(2006.01)n, *C10N40/08*(2006.01)n, *C10N40/26*(2006.01)n, *C10N40/32*(2006.01)n

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

Continuation of B. FIELDS SEARCHED
Electronic data base consulted during the international search
(name of data base and, where practicable, search terms used)

JDreamIII & keyword: JUNKATSU, SEIBUNKAI, ESUTERU, KIYU (in Japanese) and related terms

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2005213451 A **[0004]**