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(54) **BIODEGRADABLE LUBRICATING OIL COMPOSITION**

(57) [PROBLEMS] To provide a biodegradable lubricating oil composition which has excellent biodegradability, a high viscosity index, a low pour point, a high flash point, being satisfactory with lubricity, oxidative stability, property of preventing the corrosion of iron and non-ferrous metals, and suitability for use with sealing materials.

[MEANS FOR SOLVING THE PROBLEMS] A biodegradable lubricating oil composition comprising (A) a synthetic ester base oil comprising at least 50 mass% hindered ester of an aliphatic monocarboxylic acid with an aliphatic hindered polyol which has one or more qua-

ternary carbon atoms per molecule and in which at least one of the quaternary carbon atoms has one to four methylol groups bonded thereto and (B) ingredients which are (a) 0.1 to 5.0 mass% phenolic antioxidant, (b) 0.01 to 2.0 mass% calcium sulfonate having a low base number, and (c) 0.01 to 1.0 mass% triazole compound, and has the degree of biodegradation of 60 % or higher when examined by the test for the degree of microbial degradation of chemical substances according to the OECD Test Guideline 301C method.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a biodegradable lubricating oil composition. More specifically, it relates to a synthetic ester-based biodegradable lubricating oil composition which has excellent biodegradability, a high viscosity index, a low pour point, a high flash point, being satisfactory with lubricity, oxidative stability, property of preventing the corrosion of iron and non-ferrous metals, and suitability for use with sealing materials.

BACKGROUND ART

[0002] In recent years, considerable attention has been paid to a biodegradable lubricating oil in the field of lubricant application due to environmental pollution-control measures. Research and development was started and commercially available products were manufactured in this field from early 1990's in Japan. However, biodegradable lubricating oils have not widely been used in Japan because of their higher cost compared with conventional mineral oil-based lubricating oils, in spite of high attention. Japan is far behind European countries where use of a biodegradable lubricating oil is made compulsory by law.

Vegetable oils such as rapeseed oil, synthetic esters and polyalkyleneglycols have been used as a biodegradable base oil. However, vegetable oils have a problem of thermal or oxidative instability as well as unstable supply despite low cost, and polyalkyleneglycols have a problem of a poor suitability for use with sealing materials despite low cost and good thermal stability. Therefore, although synthetic esters are becoming more popular as biodegradable lubricating oils in Japan, they still have a substantial weakness against a mineral oil-based lubricating oil in terms of the cost and oxidative stability.

[0003] Japan Environment Association has authorization standard, named "ECOMARK", for biodegradable hydraulic fluids. The authorization standard was drastically revised in July, 1998 for further severe control. The major changes were as follows:

- (1) The biodegradability standard was changed from the partial biodegradation test, "CEC Test Guideline" (reference degree of biodegradability: 67% or more) to the inherent biodegradation test, "OECD Test Guideline 301C method" (reference degree of biodegradability: 60% or more), and
- (2) The acute toxicity test for Japanese medaka (*Oryzias latipes*), JIS K 0102 (reference: $LC_{50} \geq 100$ mg/L) was added.

The following examples of a biodegradable lubricating oil have been disclosed:

A lubricating oil composition comprising a polyol ester base oil composed of a carboxylic acid having 5 to 14 carbon atoms and a carboxylic acid having 15 to 38 carbon atoms in a weight ratio of 0.1:99.9 to 50:50, in which at least one of the compounds selected from the group consisting of a sulfonate, a condensate between an alkanolamine and a carboxylic acid having 5 to 14 carbon atoms and a polybutenyl succinimide is contained at 0.1 to 15 weight% (for example, Patent Document 1), a fire-resistant hydraulic fluid comprising a hydraulic base oil containing, as a main component, a polyol partial ester having a hydroxyl value of 35 mg KOH/g or more, a flash point of 290°C or more and a number-average molecular weight of 600 to 1500, wherein the ester is composed of a polyol having 3 to 12 carbon atoms and 3 to 6 total hydroxyl groups and a linear-chain monocarboxylic acid having 6 to 22 carbon atoms (for example, Patent Document 2), a lubricating oil comprising a synthetic ester having a kinematic viscosity of 20 to 40 mm²/s at 40°C, a viscosity index of 120 or more and a pour point of -30°C or less, wherein the ester is composed of a dimethylol alkane wherein the alkane has 5 to 7 carbon atoms and a linear-chain fatty acid having 10 to 20 carbon atoms (for example, Patent Document 3), a non-aqueous hydraulic fluid comprising a base oil composed of trimethylolpropane trioleate or neopentylglycol dioleate and a surfactant such as polyoxyethylene alkyl ether (for example, Patent Document 4) and the like.

[0004] Although the above-mentioned biodegradable lubricating oils are satisfactory with respect to lubricity and oxidative stability, they still have problems of a high pour point, substantial metal dissolution of non-ferrous metals used for materials for hydraulic machinery, extreme swelling of sealing materials, and so on.

[0005]

Patent Document 1: JP Kokai 1993-339591

Patent Document 2: JP Kokai 1994-228579

Patent Document 3: JP Kokai 1997-249889

Patent Document 4: JP kokai 1999-323373

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] The present invention was completed under these circumstances with an object to provide a biodegradable lubricating oil composition which has excellent biodegradability, a high viscosity index, a low pour point, a high flash point, being satisfactory with lubricity, oxidative stability, property of preventing the corrosion of iron and non-ferrous metals, and suitability for use with sealing materials.

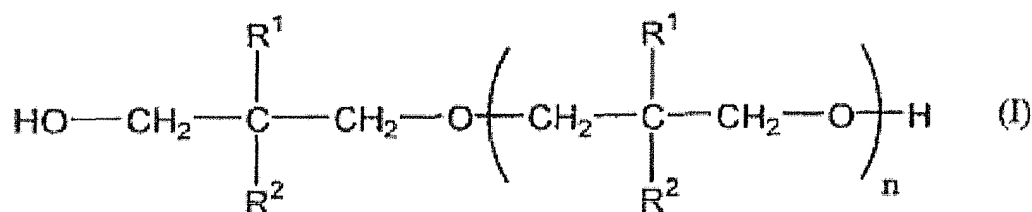
MEANS FOR SOLVING THE PROBLEMS

[0007] The present inventor studied intensively in order to develop a biodegradable lubricating oil composition which meets the aforementioned preferable properties, and found that a lubricating oil composition having a certain value or more of the biodegradability that is determined according to the OECD Test Guideline 301C method satisfies the purpose of the study, wherein the lubricating oil composition is composed of a synthetic ester base oil comprising mainly an ester composed of an aliphatic hindered polyol having a specific structure and an aliphatic monocarboxylic acid, to which a specific additive is admixed in a predetermined ratio. The present invention has been accomplished based on the aforementioned findings. That is, the present invention provides:

- (1) A biodegradable lubricating oil composition comprising (A) a synthetic ester base oil comprising at least 50 mass% hindered ester of an aliphatic monocarboxylic acid with an aliphatic hindered polyol which has one or more quaternary carbon atoms per molecule and in which at least one of the quaternary carbon atoms has one to four methylol groups bonded thereto and (B) ingredients which are (a) 0.1 to 5.0 mass% phenolic antioxidant, (b) 0.01 to 2.0 mass% calcium sulfonate having a low base number, and (c) 0.01 to 1.0 mass% triazole compound, and has the degree of biodegradation of 60 % or higher when examined by the test for the degree of microbial degradation of chemical substances according to the OECD Test Guideline 301C method,
- (2) The biodegradable lubricating oil composition according to the aforementioned (1), wherein the 96-h LC₅₀ value of the acute toxicity test for Japanese medaka (*Oryzias latipes*) according to the JIS K 0102 test method is 100 mg/L or more,
- (3) The biodegradable lubricating oil composition according to the aforementioned (1) or (2) wherein a viscosity index is 130 or more, a pour point is -40°C or less, and a flash point is 250°C or more,
- (4) The biodegradable lubricating oil composition according to any of the aforementioned (1) to (3), wherein the aliphatic hindered polyol is a compound represented by general formula (I):

[0008]

[Formula 1]



[0009] (wherein R¹ and R² represent independently a hydrocarbon group having 1 to 6 carbon atoms or a methylol group, and n is an integer of 0 to 4),

- (5) The biodegradable lubricating oil composition according to the aforementioned (4), wherein the aliphatic hindered polyol is trimethylolpropane, neopentyl glycol, pentaerythritol, or a dehydrated condensate thereof,
- (6) The biodegradable lubricating oil composition according to any of the aforementioned (1) to (5), wherein the

aliphatic monocarboxylic acid is a saturated or unsaturated monocarboxylic acid having 6 to 22 carbon atoms,
 (7) The biodegradable lubricating oil composition according to any of the aforementioned (1) to (6), wherein the calcium sulfonate as the component (B) (b) having a low base number has the total base number in the range from 0 to 100 mg KOH/g, and

(8) The biodegradable lubricating oil composition according to any of the aforementioned (1) to (7), which contains 0.1 to 5.0 mass% of an extreme-pressure agent and/or an antiwear agent as a component (B) (d).

ADVANTAGES OF THE INVENTION

[0010] According to the present invention, there is provided a synthetic ester-based biodegradable lubricating oil composition which has excellent biodegradability, a high viscosity index, a low pour point, a high flash point, being satisfactory with lubricity, oxidative stability, property of preventing the corrosion of iron and non-ferrous metals, and suitability for use with sealing materials.

BEST MODE FOR CARRYING OUT THE INVENTION

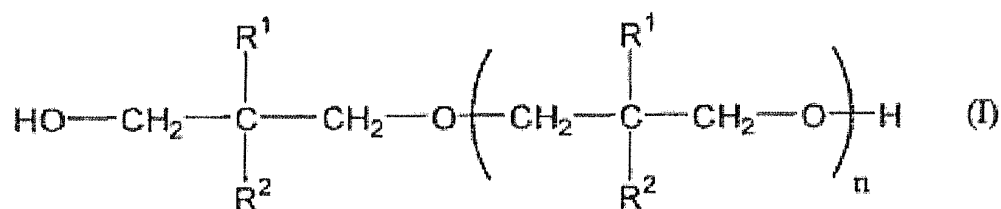
[0011] The biodegradable lubricating oil composition of the present invention comprises; (A) a synthetic ester base oil and (B) ingredients comprising a combination of (a) a phenolic antioxidant, (b) calcium sulfonate having a low base number and (c) a triazole compound.

The synthetic ester base oil used as component (A) of the present invention comprises at least 50 mass% hindered ester of an aliphatic monocarboxylic acid with an aliphatic hindered polyol which has one or more quaternary carbon atoms per molecule and in which at least one of the quaternary carbon atoms has one to four methylol groups bonded thereto.

The aliphatic hindered polyol which has one or more quaternary carbon atoms per molecule and in which at least one of the quaternary carbon atoms has one to four methylol groups bonded thereto of the present invention (which may be referred to simply as the hindered polyol hereinafter) is preferably a compound represented by general formula (I):

[0012]

[Formula 2]



[0013] (wherein R^1 and R^2 independently represent a hydrocarbon group having 1 to 6 carbon atoms or a methylol group, and n is an integer of 0 to 4.)

As the hydrocarbon group having 1 to 6 carbon atoms among R^1 and R^2 in general formula (I), a linear or branched alkyl or alkenyl group is preferable, and especially, an alkyl group is preferable.

[0014] The compound represented by general formula (I) (hindered polyols) refers to a hindered polyol such as neopentyl glycol, trimethylolalkane (the alkane has 2 to 7 carbon atoms) and pentaerythritol or a dehydrated condensate thereof. Specific examples 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-undecanediol; 2,2,6,6,10,10,14,14-octamethyl-4,8,12-trioxa-1,15-pentadecanediol; 2,6-dihydroxymethyl-2,6-dimethyl-4-oxa-1,7-heptanediol; 2,6,10-trihydroxymethyl-2,6,10-trimethyl-4,8-dioxa-1,11-undecanediol; 2,6,10,14-tetrahydroxymethyl-2,6,10,14-tetramethyl-4,8,12-trioxa-1,15-pentadecanediol; di(pentaerythritol); tri(pentaerythritol); tetra(pentaerythritol); penta(pentaerythritol) and the like.

[0015] The hindered polyols may be used singly or as a mixture of 2 or more thereof in the esterification. In the above-described general formula (I), a preferable number of n is 0 to 2.

Preferred hindered polyols are trimethylolpropane, neopentyl glycol, pentaerythritol and dehydrated condensates thereof, wherein preferable dehydrated condensates are bimolecular or trimolecular condensates.

The above-described hindered polyols can be synthesized according to the conventional method. Also, the dehydrated condensates of the hindered polyols can be synthesized by dehydration condensation of the hindered polyols in the presence of a catalyst at about 180°C by heating the hindered polyols at a temperature above the melting point and dispersing them in a solvent.

[0016] On the other hand, as the aliphatic monocarboxylic acids used in the esterification of the aliphatic hindered polyols mentioned above, saturated or unsaturated monocarboxylic acids having 6 to 22 carbon atoms are used preferably. The acyl group of the monocarboxylic acids may be linear or branched. Examples of the aliphatic monocarboxylic acids include linear saturated monocarboxylic 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, linear unsaturated monocarboxylic acids such as undecenoic acid, oleic acid, elaidic acid, cetoleic acid, erucic acid, brassidic acid, linoleic acid and linolenic acid, branched saturated monocarboxylic 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, and the like. The aliphatic monocarboxylic acids may be used singly or as a mixture of two or more kinds in the esterification.

[0017] The hindered ester synthesized by esterification reaction of the above-mentioned hindered polyol with the aliphatic monocarboxylic acid may be a fully-esterified or partially-esterified compound. A preferable hindered ester is the fully-esterified compound.

The hindered esters may be used singly or as a mixture of two or more thereof in the biodegradable lubricating oil composition of the present invention. Further, the amount of the hindered ester in the synthetic ester base oil is 50 mass% or more, preferably 70 mass% or more, and furthermore preferably 80 mass% or more in order to satisfy the predetermined properties of the biodegradable lubricating oil composition described below.

As a synthetic ester base oil which can be used together with the hindered ester, there may be cited an ester composed of an aliphatic polyol other than the hindered polyol mentioned above and the above-described monocarboxylic acid from the viewpoint of biodegradability, etc. of the lubricating oil composition.

Kinematic viscosity of the synthetic ester base oil used as the component (A) in the lubricating oil composition depends on the purpose of use of the lubricating oil composition, and is approximately in the range from 10 to 200 mm²/s at 40°C in general, preferably in the range from 10 to 100 mm²/s, and more preferably in the range from 15 to 80 mm²/s in the case of hydraulic fluid application.

An acid value of the synthetic ester base oil is preferably 3 mg KOH/g or less and particularly preferably 1 mg KOH/g or less in terms of prevention of corrosion of machinery. Further, there is no particular limitation for a hydroxyl value, but it is preferably 50 mg KOH/g or less and particularly preferably 20 mg KOH/g or less from a viewpoint of lubricity.

[0018] In the lubricating oil composition of the present invention, phenolic antioxidant as component (a) of the ingredient (B) is not particularly limited, and phenolic antioxidant known in the art can be used with suitable selection. Examples of the phenolic antioxidant include 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-t-nonylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol); 2,2'-methylenebis(4-methyl-6-cyclohexylphenol); 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butyl-ethylphenol; 2,4-dimethyl-6-t-butylphenol; 2,6-di-t-amyl-p-cresol; 2,6-di-t-butyl-4-(N,N'-dimethylaminomethylphenol); 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; n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate; 2,2'-thio[diethyl-bis-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] and the like. Among them, those of bisphenol-based and ester-containing phenols are preferable.

[0019] In the present invention, these phenolic antioxidants may be used singly or in a combination of two or more thereof. The aforementioned hindered ester used for the synthetic ester base oil has satisfactory oxidative stability by itself, and the oxidative stability of the lubricating oil composition can further be improved by admixing such a phenolic antioxidant, which also results in the increase in thermal stability. The amount of the phenolic antioxidant added is in the range from 0.1 to 5.0 mass% based on the total amount of the present composition. When the amount of the phenolic antioxidant is in the range mentioned above, the effect of improvement in the oxidative stability is exhibited and the balance between cost and effectiveness becomes excellent. The preferable amount of the phenolic antioxidant admixed is in the range from 0.5 to 3.0 mass%. In addition, although the effect of improvement in the oxidative stability can be obtained by adding an amine-based antioxidant as well, the phenolic antioxidants are used in the present invention from a viewpoint of impact on ecosystems.

[0020] In the lubricating oil composition of the present invention, the low base number calcium sulfonate as the component (b) in the ingredient (B) is added to give anti-rust effect to the lubricating oil composition and has also detergency and dispersion function. The calcium sulfonate is a calcium salt of a sulfonated alkyl-substituted aromatic compound. When the base number of the calcium sulfonate is too large, its solubility in the synthetic ester base oil is

not sufficient. Therefore, the calcium sulfonate having a low base number such that the total base number (TBN) is in the range from 0 to 100 mg KOH/g (preferably in the range from 0 to 50 mg KOH/g) is used in the present invention.

The low base number calcium sulfonates may be used singly or in a combination of two or more thereof. The amount of the calcium sulfonate added is in the range from 0.01 to 2.0 mass% based on the total amount of the composition.

When the amount of the low base number calcium sulfonate is in the range described above, satisfactory rust-prevention effect can be exhibited and excellent balance between cost and effectiveness is obtained. The amount of the low base number calcium sulfonate is preferably in the range from 0.05 to 1.0 mass%.

[0021] In the lubricating oil composition of the present invention, the triazole compound as (c) component in the ingredient (B) is added as a metal deactivator and is used to give corrosion-prevention effect for non-ferrous metals to the lubricating oil composition. Examples of the triazole compounds are benzotriazole and its derivatives. The triazole compound may be used singly or in a combination of two or more kinds thereof. The amount of the triazole compound admixed is in the range from 0.01 to 1.0 mass% based on the total amount of the composition. When the amount of the triazole compound is in the aforementioned range, satisfactory corrosion-prevention effect can be exhibited and excellent balance between cost and effectiveness is obtained. The amount of the triazole compound admixed is preferably in the range from 0.05 to 0.5 mass%.

In the lubricating oil composition of the present invention, the base oil itself has a level of lubricity equivalent to that of a conventional mineral oil-based antiwear hydraulic fluid, and in order to further improve the lubricity, an extreme-pressure agent and/or an antiwear agent may be added.

As the extreme-pressure agent, sulfur-based or phosphorus-based extreme-pressure agents can be used. Examples of the sulfur-based extreme-pressure agent are sulfurized fats and oils, sulfurized fatty acids, sulfurized esters, polysulfides, sulfurized olefins, thiocarbamates, thioterpenes, dialkylthiodipropionates and the like. Among them, sulfurized fats and oils, polysulfides and sulfurized olefins are preferred.

Examples of the phosphorus-based extreme-pressure agent are phosphates, (mono-, di-, or tri-)thiophosphates, amine salts of acidic phosphates, amine salts of (mono-, or di-)thiophosphates, phosphites, (mono-, di-, or tri-)thiophosphites and the like.

On the other hand, examples of the antiwear agent are zinc dithiophosphate (ZnDTP), zinc dithiocarbamate (ZnDTC), sulfurized molybdenum dithiophosphate (MoDTP), sulfurized molybdenum dithiocarbamate (MoDTC), and the like.

[0022] The extreme-pressure agent or antiwear agent may be used singly or in a combination of two or more kinds thereof. Further, the total amount of these agents admixed is in the range from 0.1 to 5.0 mass% based on the total amount of the composition. When the amount of the extreme-pressure agent and/or antiwear agent is in the aforementioned range, improvement in the antiwear effect is exhibited and excellent balance between cost and effectiveness is obtained. The amount of the extreme-pressure agent and/or antiwear agent is preferably in the range from 0.5 to 3.0 mass%.

In addition to the above-described additives, other additives such as viscosity index improver, pour point depressant, ash-free dispersant, surfactant, anti-foaming agent, demulsifier and so on can be added in such a range of the amount that no drawback to the effect of the present invention brought about.

[0023] The properties of the biodegradable lubricating oil composition of the present invention are explained below. The degree of biodegradation of the lubricating oil composition as determined by the microbial degradation test of chemical substances according to the OECD Test Guideline 301C method is 70 % or more (the reference degree of biodegradability is 60 % or more), and has excellent biodegradability. Further, the 96-h LC₅₀ value of the acute toxicity test for usually 100 mg/L or more, and has low impact on living organisms. Therefore, it can be said that the lubricating oil composition is a very environmentally friendly lubricating oil.

Also, the viscosity index is usually 130 or more, preferably 140 or more, the pour point is -40°C or lower, preferably -45°C or lower, and the flash point is usually 250°C or higher, preferably 260°C or higher. The synthetic ester base oil of the aforementioned component (A) has a viscosity index of 130 or more by itself, so addition of a viscosity index improver to the present composition is usually not necessary.

The lubricating oil composition has such a low pour point as mentioned above so that machinery startability at lower temperatures is excellent with the present composition when it is used as a hydraulic fluid. Also, the present composition has such a high flash point as mentioned above so that it has high flame retardance and hence it belongs to the category of a safe combustible liquid having VG of 32 or more according to the Fire Service Law.

[0024] The biodegradable lubricating oil composition of the present invention has excellent biodegradability, low impact to ecosystems, a high viscosity index, a low pour point, a high flash point, being satisfactory with lubricity, oxidative stability, property of preventing the corrosion of non-ferrous metals, and suitability for use with sealing materials. It has thus an excellent balance of those different properties.

The lubricating oil composition is preferable, for example, as a hydraulic fluid that is a power transmission fluid used in power transmission, power control, shock absorption and the like in a hydraulic system such as hydraulic machinery or equipment, a lubricating oil for automobiles used in automatic transmission, buffer, driving machinery such as power steering, gears and the like, a metal-working oil for cutting, polishing or plasticizing, and the like.

EXAMPLES

[0025] The present invention is further described by the following examples but not limited thereto. In addition, properties of the lubricating oil composition in each example were determined by the following methods:

(1) General Properties:

- (a) Kinematic viscosity at 40°C: Determined according to JIS K 2283 test method.
- (b) Viscosity index: Determined according to JIS K 2283 test method.
- (c) Acid value: Determined according to JIS K 2501 test method.
- (d) Hydroxyl value: Determined by the pyridine-acetyl chloride method according to JIS K 0070 test method.
- (e) Flash point: Determined by using the Cleveland Open Cup (COC) tester according to JIS K 2265 test method.
- (f) Pour point: Determined according to JIS K 2269 test method.
- (g) Antirust performance: Determined according to JIS K 2510 test method, wherein the rust formation after 24 hours of the test initiation was inspected by visual observation using distilled water at 60°C.

[0026]

(2) Biodegradability:

The degree of biodegradation was determined according to the modified MITI test method, OECD301C. According to the authorized standard of "ECOMARK" revised in July, 1998, the degree of biodegradation is required to be 60 % or more.

(3) Acute toxicity to fish:

The half lethal concentration (LC₅₀) after 96 hours was determined according to JIS K 0102 test method using Japanese medaka (*Oryzias latipes*). According to the authorized standards of "ECOMARK" revised in July, 1988, the LC₅₀ value is required to be 100 mg/L or more.

(4) Lubricity:

- (a) Shell Four-ball EP test (ASTM D2783): The load wear index (LWI) was determined from the last non-seizure load (LNL) and weld load (WL) values under the conditions including 1800 rpm and room temperature. The higher the LWI value, the better the load resistance.
- (b) Shell Four-ball wear test (ASTM D2783): The wear spot size was determined under the conditions including 1200 rpm, load of 294 N, temperature of 50°C and 30 minute test duration.
- (c) FZG Scouring test: The load stage of scouring was determined according to ASTM D5182-91 test method under the conditions including 90°C, 1450 rpm, 15 minute test duration, using the A-type gear.
- (d) Vane pump test (according to ASTM D2882): The degree of wear of vane and cam ring was determined by using a vane-type pump (Vickers Inc., V-104C Pump) after 250 hour operation under the conditions including 65°C, 13.7 MPa, 1200 rpm, 60 L oil volume and a flow rate of about 25 L/min.

[0027]

(5) Oxidative stability:

(a) IOT:

The relative kinematic viscosity at 40°C (kinematic viscosity after the test/kinematic viscosity before the test) was determined, wherein 300 mL of a sample oil filled in a cylinder (45 mm in diameter, 500 mm in length) was subjected to a test in the presence of copper and iron as a catalyst, under the conditions either at 130°C for 48 hours or at 150°C for 48 hours with air intake rate of 10 L/hour.

(b) High pressure circulation test:

The relative kinematic viscosity at 40°C (kinematic viscosity after the test/kinematic viscosity before the test) was determined after a test sample was subjected to a test under the following conditions:

Pump type: (UCHIDA-RFXROTH "A2FO-10/ 61R-PPB06"),

Pump pressure: 35 MPa,
 Oil flow rate: 13.6 L/min,
 Oil temperature: 80°C,
 Air intake rate: 1 NL/h,
 Catalyst: Cu coil (1.6 mm in diameter, 60 m in length), and
 Test duration: 600 h.

Further, in the test described above, durability test was performed without limiting the test duration to measure the time when either the relative kinematic viscosity the test duration to measure the time when either the relative kinematic viscosity reaches 1.1, or the acid value reaches 2.0 mg KOH/g, or the Millipore value reaches 10 mg/100 mL of the sample (wherein the Millipore value is defined as a weight of fine powdery residue obtained by filtering out the residue with 0.8 µm membrane filter by vacuum filtration, followed by washing with n-hexane and drying), from which the service life was determined.

[0028]

(6) Corrosion prevention for non-ferrous metals:

After conducting a high-pressure circulation test for 600 hours in the manner similar to the aforementioned test (5), amounts of copper (dissolved from the catalyst) and zinc (dissolved from the piping material) in the sample oil were measured. In parallel to this method, a metal immersion test was also carried out according to the following procedure:

- (a) Put 100 g of a sample oil in a 200 mL mayonnaise bottle,
- (b) Weigh the test piece after polishing with sandpaper #240, washing with gasoline and drying,
- (c) Put one test piece into one sample bottle and heat at 100°C for 168 hours in a temperature-controlled bath,
- (d) Take out the test piece, wipe off the sample oil on the test piece using waste cloth, wash with gasoline, dry and weigh.

At this time, a metal immersion test as described above was carried out on a zinc test piece (1.0 mm x 26 mm x 60 mm) for the oil sample used in Comparative example 6, a weight loss of 0.47 % was observed.

[0029]

(7) Suitability for use with sealing material:

An immersion test was performed according to the JIS K 6258 method for nitrile-butadiene rubber (NBR) and polyurethane at 100°C for 240 hours and at 120°C for 240 hours, respectively, and the rate of change after the test with respect to values before the test was determined for each property: [mass change rate (%), volume change rate (%), hardness change (no units), change rate of tensile strength (%), and change rate of elongation at break (%)].

Here, judgment criteria for evaluation of each of the aforementioned properties are as follows:

◎ (excellent), ○ (good), △ (normal), and × (poor).

[0030] Examples 1 to 3 and Comparative examples 1 to 8

(1) Lubricating oil compositions with compositions shown in Tables 1-1 and 1-2 were prepared along with commercially-available products. General properties and biodegradability of these lubricating oil compositions are listed in Tables 2-1 and 2-2.

[0031] Table 1

Table 1-1

	Examples			Comparative examples		
	1	2	3	1	2	3
Prepared product or commercial product	Prepared oil	Prepared oil	Prepared oil	Commercial oil A	Commercial oil B	Commercial oil C
Type of base oil	Ester	Ester	Ester	Ester	Ester	Ester
Base oil (mass%)	Hindered ester	PET Ester 31.6	TMP Ester 90.8	NPG dioleate 2.0 parts	NPG dioleate 3.0 parts	-
		TMP trioleate 66.2	TMP trioleate 6.5	TMP trioleate 8.0 parts	TMP trioleate 8.0 parts	-
		-	-	-	PET tetraoleate 1.0 part	-
Non-hindered ester	-	-		Aliphatic ester	Aliphatic ester	Rapeseed oil
Total	97.8	97.3	97.3			
Antioxidant (mass%)	Phenolic 1.4	Phenolic 1.4	Phenolic 1.4	Phenolic	Amine-based	Phenolic
Antirust agent (mass%)	Low base number Ca sulfonate 0.1	Low base number Ca sulfonate 0.1	Low base number Ca sulfonate 0.1	-	-	-
Metal deactivator (mass%)	Benzotriazole-based 0.1	Benzotriazole-based 0.1	Benzotriazole-based 0.1	-	-	-
Extreme-pressure agent or antiwear agent (mass%)	-	S, P type 10	S, P type 1.0	ZnDTP	Oleic acid, P type	Oleic acid, P type
Other additives (mass%)	Methacrylate anti-foaming agent 0.6	Anti-foaming agent 0.1	Anti-foaming agent 0.1	Large base-number Ca sulfonate, imide-based friction modifier	POE alkylether	-

[0032] Table 2

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Table 1-2

Prepared product or commercial product	Comparative examples				
	4	5	6	7	8
Type of base oil	Commercial oil D	Commercial oil E	Commercial oil F	Prepared oil	Commercial oil G
Base oil (mass%)	Ester	Ester	Ester	Ester	Mineral oil-based
	Hindered ester	TMP isostearate, oleate (partially-esterified)	2-butyl-2-ethyl-1,3-prop ane diol laurate and oleate mixture	TMP trioleate 98.85	-
	-			-	-
	-			-	-
Non-hindered ester	Diisotridecyladipate	-		-	-
Total				98.85	
Antioxidant (mass%)	Amine-based	Amine-based 1.0	Phenolic	Amine-based 1.0	Phenolic, amine-based
Antirust agent (mass%)	-	Low base number Ca sulfonate 0.1	-	Low base number Ca sulfonate 0.1	Polyol alkenyl succinate
Metal deactivator (mass%)	-	Benzotriazole-based 0.05	-	Benzotriazole-based 0.05	Triazole-based
Extreme-pressure agent or antiwear agent (mass%)	S, P type	-	Oleic acid	-	Tricresyl phosphate
Other additives (mass%)	Polybutene polymer	Polymethacrylate	-	-	Various additives*1
*1 Various additives: a pour point depressant, detergent dispersant, anti-foaming agent, demulsifier, etc.					

[0033] Note:

In Tables 1-1 and 1-2, PET denotes pentaerythritol, TMP denotes trimethylolpropane, NPG denotes neopentyl glycol, ZnDTP denotes zinc dithiophosphate, and POE denotes polyoxyethylene.

[0034] Table 3

Table 2-1

		Examples			Comparative examples		
		1	2	3	1	2	3
General properties	Kinematic viscosity @ 40°C (mm ² /s)	45.7	31.9	21.9	41.2	46.4	38.4
	Viscosity index	175	170	141	179	170	213
	Acid value (mg KOH/g)	0.84	0.95	0.78	0.78	1.55	0.80
	Hydroxyl value (mg KOH/g)	3 >	3 >	3.6	10.6	39.5	3 >
	Flash point (°C)	312	278	260	286	288	316
	Pour point (°C)	-50.0>	-50.0	-50.0	-37.5	-37.5	-32.5
	Rust prevention	No rust	No rust	No rust	Slight rust	No rust	No rust
	Evaluation	◎	◎	◎	○	◎	◎
Biodegradability	Degree of microbial degradation (%) [OECD 301C]	77	78	83	63	-	-
	Acute toxicity to Japanese medaka [96-h LC ₅₀] (mg/L)	100 <	100 <	100 <	-	-	-
	Evaluation	◎	◎	◎	○ Ecomark product	Ecomark product	Ecomark product

[0035] Table 4

Table 2-2

		Comparative examples				
		4	5	6	7	8
General properties	Kinematic viscosity @ 40°C (mm ² /s)	49.7	67.9	29.6	45.9	45.4
	Viscosity index	153	162	150	188	108
	Acid value (mg KOH/g)	0.18	0.23	3.60	0.29	0.06
	Hydroxyl value (mg KOH/g)	3 >	38.2	25.2	5.2	3 >
	Flash point (°C)	260	294	250	318	238
	Pour point (°C)	−50.0 >	−42.5	−35.0	−50.0	−32.5
	Rust prevention	Medium degree of rust	No rust	Slight rust	Slight rust	No rust
	Evaluation	△	⊙	△	△	○
Biodegradability	Degree of microbial degradation (%) [OECE 301C]	-	-	-	66	20 > (Estimated)
	Acute toxicity to Japanese medaka [96-h LC ₅₀] (mg/L)	-	-	-	100 <	-
	Evaluation	Ecomark product	Biodegradable	Ecomark product	○	×

[0036] (2) Tables 3-1 and 3-2 indicate the test results of lubricity, oxidative stability and corrosion prevention of non-ferrous metals for each lubricating oil composition.

[0037] Table 5

Table 3-1

		Examples			Comparative examples		
		1	2	3	1	2	3
5 10 15	Lubricating oil composition	<Shell four-ball EP test> Last non-seizure load (N)	490	618	618	490	785
		Weld load (N)	1236	1961	1569	1961	1569
		Load wear index (N)	214	326	264	241	332
		<Shell four-ball wear test> Wear spot size (mm)	0.58	0.34	0.33	0.29	0.32
		<FZG scouring test> Load stage	8	11	-	-	-
		<Vane pump test> Amount of wear (mg)	17	18	-	-	-
		Evaluation	○	◎	○	○	◎
20	Oxidative stability	<IOT> Relative kinematic viscosity 130°C, 48 h	1.05	1.08	1.01	1.08	1.28
		150°C, 48 h	1.47	1.44	1.09	1.4	2.05
		<High pressure circulation test> Relative kinematic viscosity	1.11	-	-	1.08	1.13
		Life (h)	600	-	-	800	500
		Evaluation	○	-	-	○	△
25	Corrosion prevention	<High pressure circulation test> Cu dissolution in oil (ppm)	2 >	-	-	180	5
		Zn dissolution in oil (ppm)	2 >	-	-	*1	231
		Evaluation	◎	-	-	×	×

*1: A value of Zn dissolution was not determined because of the addition of ZnDTP.

[0038] Table 6

Table 3-2

		Comparative examples				
		4	5	6	7	8
5	Lubricating oil composition	<Shell four-ball EP test>				
		Last non-seizure load (N)	981	490	392	392
		Weld load (N)	1961	1236	1236	1236
		Load wear index (N)	424	206	181	173
		<Shell four-ball wear test>				
		Wear spot size (mm)	0.39	0.65	0.28	0.58
10		<FZG scouring test>				
		Load stage	-	-	-	-
		<Vane pump test>				
		Amount of wear (mg)	-	21	-	39
15	Oxidative stability	<IOT>				
		Relative kinematic viscosity				
		130°C, 48 h	1.03	1.12	-	1.18
		150°C, 48 h	1.04	1.29	-	1.66
		<High pressure circulation test>				
		Relative kinematic viscosity	0.98	0.98	-	1.06
20		Service life (h)	500	600	-	900
		Evaluation	○	△	-	△
25	Corrosion prevention	<High pressure circulation test>				
		Cu dissolution in oil (ppm)	2 >	27	-	2 >
		Zn dissolution in oil (ppm)	2 >	169	*2	2 >
		Evaluation	◎	×	×	◎

*2: Substantial corrosion found by the immersion test at 100°C, 168 h.

[0039] (3) Table 4 indicates the test results of suitability for use with sealing materials of the lubricating oil composition of Example 1 and the lubricating oil compositions of Comparative examples 1 to 4.

[0040] Table 7

Table 4

			Examples	Comparative examples			
			1	1	2	3	4
Suitability for use with sealing materials	NBR (ISO SRE NBR/L) (%)	Change of volume	39	40	64	42	100
		Change of weight	30	29	48	31	75
		Change of hardness	-28	-28	-39	-31	-55
		Change of elongation	-34	-29	-43	-32	-50
		Change of tensile strength	-42	-29	-59	-39	-82
	Polyurethane (U-801) (%)	Change of volume	0	0	-1	-2	5
		Change of weight	1	0	-3	-2	4
		Change of hardness	0	-18	-10	-10	0
		Change of elongation	34	56	-92	44	36
		Change of tensile strength	-13	-32	-85	-63	-47
	Evaluation		◎	○	△	○	△

[0041] As is evident from the results of Tables 1 to 4, the lubricating oil compositions of the present invention (Examples 1 to 3) have a well-balanced properties such as excellent biodegradability, a high viscosity index, a low pour point, a high flash point, being satisfactory with lubricity, oxidative stability, property of preventing the corrosion of iron and non-ferrous metals, and suitability for use with sealing materials.

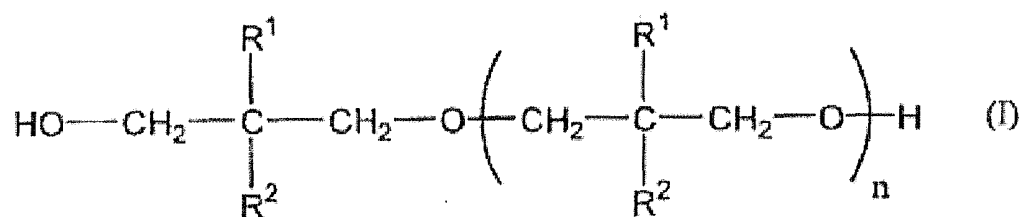
INDUSTRIAL APPLICABILITY

[0042] The biodegradable lubricating oil composition of the present invention comprises a synthetic ester base oil having excellent biodegradability, has well-balanced properties including lubricating performance, and is preferably used, for example, as a hydraulic fluid, automotive lubricating oil, metal-working oil, and so on.

Claims

1. A biodegradable lubricating oil composition comprising (A) a synthetic ester base oil comprising at least 50 mass% hindered ester of an aliphatic monocarboxylic acid with an aliphatic hindered polyol which has one or more quaternary carbon atoms per molecule and in which at least one of the quaternary carbon atoms has one to four methylol groups bonded thereto and (B) ingredients which are (a) 0.1 to 5.0 mass% phenolic antioxidant, (b) 0.01 to 2.0 mass% calcium sulfonate having a low base number, and (c) 0.01 to 1.0 mass% triazole compound, and has the degree of biodegradation of 60 % or higher when examined by the test for the degree of microbial degradation of chemical substances according to the OECD Test Guideline 301C method.
2. The biodegradable lubricating oil composition according to claim 1, wherein the 96-h LC₅₀ value of the acute toxicity test for Japanese medaka (*Oryzias latipes*) according to the JIS K 0102 test method is 100 mg/L or more.
3. The biodegradable lubricating oil composition according to claim 1 or 2, wherein a viscosity index is 130 or more, a pour point is -40°C or less, and a flash point is 250°C or more.
4. The biodegradable lubricating oil composition according to any of claims 1 to 3, wherein the aliphatic hindered polyol is a compound represented by general formula (I):

[Formula 1]



(wherein R¹ and R² represent independently a hydrocarbon group having 1 to 6 carbon atoms or a methylol group, and n is an integer of 0 to 4).

5. The biodegradable lubricating oil composition according to claim 4, wherein the aliphatic hindered polyol is trimethylolpropane, neopentyl glycol, pentaerythritol, or a dehydrated condensate thereof.
6. The biodegradable lubricating oil composition according to any of claims 1 to 5, wherein the aliphatic monocarboxylic acid is a saturated or unsaturated monocarboxylic acid having 6 to 22 carbon atoms.
7. The biodegradable lubricating oil composition according to any of claims 1 to 6, wherein the calcium sulfonate as the component (B) (b) having a low base number has the total base number in the range from 0 to 100 mg KOH/g.
8. The biodegradable lubricating oil composition according to any of claims 1 to 7, which contains 0.1 to 5.0 mass% of an extreme-pressure agent and/or an antiwear agent as a component (B) (d).

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/001216

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C10M169/04// (C10M169/04, 105:38, 105:40, 129:10, 133:38, 133:44, 135:10, 159:24), C10N10:04, 20:00, 20:02, 30:00, 30:02, 30:06, 30:08, 30:10, 30:12, 40:04, 40:08, 40:20 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) Int.Cl. ⁷ C10M169/04, 105/38-105/40, 129/10-129/14, 133/38, 133/44, 135/10, 159/24, C10N10:04, 20:00-20:02, 30:00-30:02, 30:06-30:12, 40:04, 40:08, 40:20-40:24 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 1996-2005 Kokai Jitsuyo Shinan Koho 1971-2004 Toroku Jitsuyo Shinan Koho 1994-2005 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.
X	JP 2004-18531 A (Nippon Oil Corp.), 22 January, 2004 (22.01.04), & AU 2003242313 A & WO 03/106601 A1	1-8
X	JP 2002-97485 A (Nippon Mitsubishi Oil Corp.), 02 April, 2002 (02.04.02), & CN 1346872 A & KR 2002023127 A	1-8
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X	JP 2001-234187 A (Nippon Steel Chemical Co., Ltd.), 28 August, 2001 (28.08.01), (Family: none)	1-8
☒ 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 "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 April, 2005 (26.04.05)		Date of mailing of the international search report 17 May, 2005 (17.05.05)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/001216

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 55-84396 A (Director General of Technical Research and Development Institute of Defense Agency), 25 June, 1980 (25.06.80), (Family: none)	1-8

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