(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 248 876 A1**

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

(43) Date of publication:
10.11.2010 Bulletin 2010/45

(21) Application number: **09710998.7**

(22) Date of filing: **10.02.2009**

(51) Int Cl.:
C10M 135/00 $^{(2006.01)}$
C10M 129/10 $^{(2006.01)}$
C10M 133/12 $^{(2006.01)}$
C10M 135/18 $^{(2006.01)}$
C10M 135/22 $^{(2006.01)}$
C10M 159/22 $^{(2006.01)}$
C10M 159/24 $^{(2006.01)}$
C10M 169/04 $^{(2006.01)}$
C10N 10/04 $^{(2006.01)}$
C10N 30/12 $^{(2006.01)}$
C10N 40/25 $^{(2006.01)}$

(86) International application number:
PCT/JP2009/052219

(87) International publication number:
WO 2009/101933 (20.08.2009 Gazette 2009/34)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA RS

(30) Priority: **14.02.2008 JP 2008033313**

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

(72) Inventors:
- **TESHIMA, Kazuhiro**
  Ichihara-shi
  Chiba 299-0107 (JP)
- **ISHIKAWA, Motoharu**
  Ichihara-shi
  Chiba 299-0107 (JP)

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

(54) LUBRICANT COMPOSITION

(57) A lubricating oil composition is used in an internal combustion engine that uses a fuel containing at least one fat and oil of natural fat and oil, hydrotreated natural fat and oil, transesterified natural fat and oil and hydrotreated transesterified natural fat and oil. A sulfur compound containing at least one -C-S-C-bond is added to base oil. A content of sulfur contained in the -C-S-C-bond is 0.3 mass% or less based on a total amount of the compound.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a lubricating oil composition to be used in an internal combustion engine that uses a fuel originating from natural fat and oil.

Background Art

[0002] These days, environmental regulations are being increasingly tightened on a global scale, among which fuel efficiency regulations and exhaust emission regulations for automobiles are especially being further tightened. Demands for tightening of the regulations are derived from environmental issues such as global warming and resource conservation due to a concern for depletion of petroleum resources.
Meanwhile, plants living on the earth absorb carbon dioxide in the air, water and sunlight to photosynthetically generate carbohydrate and oxygen. So-called biofuel, which is manufactured from plant-based plant oil, has been gathering remarkable attentions because of its effects on reduction of carbon dioxide (a main cause of global warming) and reduction of atmospheric contaminants emitted from automobiles. In line with an idea of carbon neutral advocating that carbon dioxide generated due to combustion of plant biomass is not counted as a contributor to an increase of the global warming gas, ratio at which the biofuel is mixed in hydrocarbon fuel is expected to be increased in the future (for instance, see Non-Patent Document 1).
[0003] Non-Patent Document 1: Koji YAMANE, BIODIESEL- From Deep Fryer to Fuel Tank (Tokyo-Tosho-Shuppankai, May of 2006)

Disclosure of the Invention

Problems to Be Solved by the Invention

[0004] An important problem in an internal combustion engine, especially in a diesel engine, has been how to reduce environment pollution caused by such emission gas components as particulate matters (PM) such as soot and NO_X. An effective solution is to mount such an exhaust purifying device as a diesel particulate filter (DPF) or an exhaust purifying catalyst (oxidization or reduction catalyst) on an automobile. For example, soot generated in the diesel engine adheres to the DPF to be removed by oxidization and combustion.
When the DPF is mounted on the diesel engine, post-injection of fuel is generally conducted so as to combust the soot accumulated on the filter. Engine oil is diluted by the fuel due to the post-injection, so that performance of the engine oil is expected to be lowered. Particularly, since biofuel can be easily accumulated in the engine oil due to its property and generates polar compounds when degraded and decomposed, the biofuel may adversely affect corrosion of engine parts such as a piston. Also, the filter is likely to be clogged by a metal oxide, hydrosulfate, carboxylate or the like generated in the combustion. In addition, since a portion of the used engine oil is combusted and exhausted as exhaust gas, it is preferable that metal content or sulfur content in lubricating oil is as low as possible. Thus, it is preferable to decrease phosphorus content or sulfur content in the lubricating oil in order to prevent degrading of exhaust gas purifying catalyst.
However, lubricating oil sufficiently adapted for use with biofuel has not been provided yet. For example, when content in the lubricating oil such as metal content, phosphorus content or sulfur content is simply reduced, lubricating performance thereof may be lowered despite the intentions. Particularly, since polar compounds are formed when biofuel is degraded and decomposed, the biofuel may accelerate corrosion of engine parts.
An object of the invention is to provide a lubricating oil composition capable of reducing corrosion of engine parts even when biofuel or biofuel-mixed fuel is used in an internal combustion engine such as a diesel engine.

Means for Solving the Problems

[0005] In order to solve the above-mentioned problems, a lubricating oil composition as follows is provided according to an aspect of the invention.

(1) A lubricating oil composition is used in an internal combustion engine that uses a fuel containing at least one fat and oil of natural fat and oil, hydrotreated natural fat and oil, transesterified natural fat and oil and hydrotreated transesterified natural fat and oil, in which a sulfur compound containing at least one -C-S-C-bond is added to base oil and a content of sulfur contained in the -C-S-C-bond is 0.3 mass% based on a total amount of the compound.
(2) The lubricating oil composition according to the aspect of the invention in which the sulfur compound does not

contain a -C-S_X-C-bond (where x is an integer of 2 or more)

(3) The lubricating oil composition according to the aspect of the invention further containing an alkaline earth metal-based detergent in an amount of 0.35 mass% or less.

(4) The lubricating oil composition according to the aspect of the invention further containing a phosphorus in an amount of 0.12 mass% or less based on the amount of the composition.

(5) The lubricating oil composition according to the aspect of the invention further containing a sulfate ash in an amount of 1.1 mass% or less.

(6) The lubricating oil composition according to the aspect of the invention further containing at least one of a phenol-based antioxidant and an amine-based antioxidant in an amount of 0.3 mass% or more based on the total amount of the composition.

(7) The lubricating oil composition according to the aspect of the invention further containing a sulfur in an amount of 0.5 mass% or less based on the total amount of the composition.

[0006] The lubricating oil composition according to the aspect of the present invention is corrosive-resistant to engine parts such as a piston in the internal combustion engine using biofuel made of natural fat and oil and the like even when the biofuel is mixed into the engine oil. In addition, in the lubricating oil composition according to the aspect of the invention, even when used in a diesel engine with a DPF, the lubricating oil composition can reduce residual ash content on the DPF, thereby preventing performance of the DPF from being deteriorated.

Natural fat and oil of the invention is not limited to plant-derived fat and oil but may include animal-derived fat and oil.

Best Mode for Carrying Out the Invention

[0007] Exemplary embodiment(s) of the invention will be described in detail below.

A lubricating oil composition according to the invention is a lubricating oil composition used in an internal combustion engine, the internal combustion engine using a fuel that contains at least one fat and oil of natural fat and oil, hydrotreated natural fat and oil, transesterified natural fat and oil and hydrotreated transesterified natural fat and oil.

[0008] Although the natural fat and oil may be a variety of animal-derived or plant-derived fat and oil that is generally available in nature, the natural fat and oil is preferably plant oil that contains ester of fatty acid and glycerin as a major ingredient, examples of which are safflower oil, soybean oil, canola oil, palm oil, palm kernel oil, cotton oil, cocoanut oil, rice bran oil, benne oil, castor oil, linseed oil, olive oil, wood oil, camellia oil, earthnut oil, kapok oil, cacao oil, haze wax, sunflower seed oil, and corn oil.

The hydrotreated natural fat and oil is formed by hydrogenating the above fat and oil under the presence of a suitable hydrogenating catalyst.

The hydrogenating catalyst is exemplified by a nickel-based catalyst, a platinum family (Pt, Pd, Rh, Ru) catalyst, a cobalt-based catalyst, a chrome-oxide based catalyst, a copper-based catalyst, an osmium-based catalyst, an iridium-based catalyst, a molybdenum-based catalyst and the like. Two or more of the catalysts may also be preferably combined to be used as the hydrogenating catalyst.

[0009] The transesterified natural fat and oil is ester formed by transesterifying triglyceride contained in the natural fat and oil under the presence of a suitable ester-synthesis catalyst. For instance, by transesterifying lower alcohol and the fat and oil under the presence of the ester-synthesis catalyst, fatty acid ester usable as biofuel is manufactured. The lower alcohol, which is used as an esterifying agent, is exemplified by alcohol having 5 or less carbon atoms such as methanol, ethanol, propanol, butanol, pentanol. In view of reactivity and cost, methanol is preferable. The lower alcohol is generally used in an amount equivalent to the fat and oil or more.

The hydrotreated transesterified natural fat and oil is formed by hydrogenating the above transesterified fat and oil under the presence of a suitable hydrogenating catalyst.

The natural fat and oil, the hydrotreated natural fat and oil, the transesterified natural fat and oil, and the hydrotreated transesterified natural fat and oil can be preferably used as mixed fuel by adding the above to fuel formed of hydrocarbon such as light oil.

[0010] Base oil used in the lubricating oil composition according to the invention is not particularly limited but may be suitably selected from any mineral oil and synthetic oil that have been traditionally used as base oil of the lubricating oil for the internal combustion engine.

Examples of the mineral oil include: mineral oil refined by processing lubricating oil fractions, which are obtained by vacuum-distilling atmospheric residual oil obtained by atmospherically distilling crude oil, by at least one of solvent-deasphalting, solvent-extracting, hydrocracking, solvent-dewaxing, catalytic-dewasing and hydrorefining; and mineral oil manufactured by isomerizing wax and GTL (gas-to-liquid) WAX.

On the other hand, examples of the synthetic oil include polybutene, polyolefin (α-olefin homopolymer or copolymer such as ethylene-α-olefin copolymer), various esters (such as polyol ester, diacid ester and phosphoric ester), various ethers (such as polyphenylether), polyglycol, alkylbenzene, and alkyl naphthalene. Among the above, polyolefin and

polyol ester are particularly preferable.
One of the above mineral oil may be singularly used or two or more thereof may be combined to be used as the base oil. In addition, one of the above synthetic oil may be singularly used or two or more thereof may be combined to be used. Further, at least one of the above mineral oil and at least one of the above synthetic oil may be combined for use.

[0011] Although viscosity of the base oil subjects to no specific limitation and varies depending on usage of the lubricating oil composition, kinetic viscosity thereof at 100 degrees C is generally preferably 2 to 30 mm^2/s, more preferably 3 to 15 mm^2/s, much more preferably 4 to 10 mm^2/s. When the kinetic viscosity at 100 degrees C is 2 mm^2/s or more, evaporation loss is small. When the kinetic viscosity at 100 degrees C is 30 mm^2/s or less, power loss due to viscosity resistance is restricted, thereby improving fuel efficiency.

[0012] As the base oil, oil whose %CA measured by a ring analysis is 3 or less and whose sulfur content is 50 ppm by mass or less can be preferably used. The %CA measured by the ring analysis means a proportion (percentage) of aromatic content calculated by the n-d-M method (a ring analysis). The sulfur content is measured based on JIS (abbreviation for Japanese Industrial Standard) K 2541.
The base oil whose %CA is 3 or less and whose sulfur content is 50 ppm by mass or less exhibits a favorable oxidation stability. Such base oil can restrict an increase of acid number and a generation of sludge, thereby providing a lubricating oil composition that is less corrosive to metal. The sulfur content is more preferably 30 ppm by mass or less. The %CA is more preferably 1 or less, further more preferably 0.5 or less.
In addition, viscosity index of the base oil is preferably 70 or more, more preferably 100 or more, much more preferably 120 or more. In the base oil whose viscosity index is 70 or more, a viscosity change due to a temperature change is small.

[0013] In the lubricating oil composition of the invention, a sulfur compound containing at least one -C-S-C-bond is added in the above-described base oil.
Such a sulfur compound is preferably dissolved or uniformly dispersed in the base oil of the lubricating oil. Examples of such sulfur compound may include sulfurized fat and oil, a sulfurized fatty acid, an ester sulfide, an olefin sulfide, a dihydrocarbyl monosulfide, a thiadiazole compound, a thiophosphate ester (thiophosphite, thiophosphate), an alkylthiocarbamoyl compound, a thiocarbamate compound, a thioterpene compound and a dialkyl thiodipropionate compound. Among these, a sulfur compound used as a sulfuric antioxidant is preferable.
Herein, the sulfurized fat and oil may be obtained by reacting fat and oil (e.g., lard oil, whale oil, vegetable oil and fish oil) with sulfur or a sulfur-containing compound. A content of the sulfur is not particularly limited, but 5 to 30 mass% is generally preferable. Concrete examples of the sulfurized fat and oil may include a surfurized lard, a sulfurized rape seed oil, a sulfurized castor oil, a sulfurized soybean oil and a sulfurized rice bran oil. The sulfurized fatty acid may be exemplified by a sulfurized oleic acid, while the ester sulfide may be exemplified by a sulfurized methyl oleate, a sulfurized rice bran fatty acid octyl and a ditridecyl thiodipropionate.

[0014] Examples of the olefin sulfide preferably used according to the invention include a compound represented by the following formula (1).

$$R^1\text{-S-}R^2 \qquad (1)$$

In the formula, R^1 represents an alkenyl group having 2 to 15 carbon atoms, and R^2 represents an alkyl group or an alkenyl group having 2 to 15 carbon atoms.
The compound can be obtained by reacting an olefin having 2 to 15 carbon atoms or a dimer to a tetramer thereof with a sulfurizing agent such as sulfur, sulfur chloride and the like. The olefin may preferably be propylene, isobutene, and diisobutene.
Examples of the dihydrocarbyl monosulfide include a compound represented by the following formula (2).

$$R^3\text{-S-}R^4 \qquad (2)$$

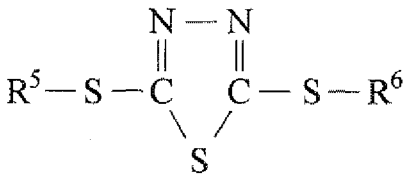
In the formula, R^3 and R^4 each represent an alkyl group or a cyclic alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an alkyl aryl group having 7 to 20 carbon atoms or an arylalkyl group having 7 to 20 carbon atoms, which may be mutually the same or different.
Herein, when R^3 and R^4 are alkyl groups, the compound is also referred to as an alkyl sulfide.

[0015] Examples of R^3 and R^4 in the formula (2) may include methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, various pentyl groups, various hexyl groups, various heptyl groups, various octyl groups, various nonyl groups, various decyl groups, various dodecyl groups, cyclohexyl group, cyclooctyl group, phenyl group, naphthyl group, tolyl group, xylyl group, benzyl group and phenethyl group.
Examples of the dihydrocarbyl monosulfide may include dibenzyl monosulfide, various dinonyl monosulfides, various didodecyl monosulfides, various dibutyl monosulfides, various dioctyl monosulfides, diphenyl monosulfide and dicyclohexyl monosulfide.
Examples of the thiadiazole compound may preferably include 1,3,4-thiadiazole, 1,2,4-thiadiazole compound, and 1,4,5-

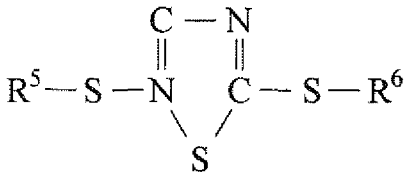
thiadiazole represented by the following formulae (3) to (5).

[0016]

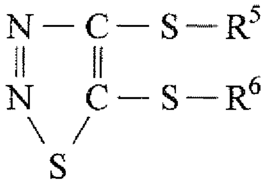
[Chemical Formula 1]



· · · · · · · (3)



· · · · · · · (4)



· · · · · · · (5)

[0017] In the formulae, R^5 to R^6 each represent a hydrocarbon group having 1 to 20 carbon atoms.

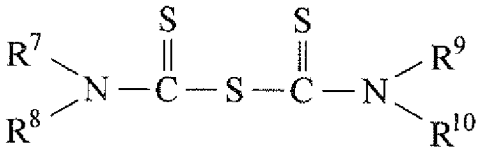
Preferable examples of the thiadiazole compound may include 2,5-bis(n-hexyldithio)-1,3,4-thiadiazole, 2,5-bis(n-octyldithio)-1,3,4-thiadiazole, 2,5-bis(n-nonyldithio)-1,3,4-thiadiazole, 2,5-bis-(1,1,3,3-tetramethylbutyldithio)-1,3,4-thiadiazole, 3,5-bis(n-hexyldithio)-1,2,4-thiadiazole, 3,5-bis(n-octyldithio)-1,2,4-thiadiazole, 3,5-bis(n-nonyldithio)-1,2,4-thiadiazole, 3,5-bis-(1,1,3,3-tetramethylbutyldithio)-1,2,4-thiadiazole, 4,5-bis(n-hexyldithio)-1,2,3-thiadiazole, 4,5-bis(n-octyldithio)-1,2,3-thiadiazole, 4,5-bis(n-nonyldithio)-1,2,3-thiadiazole and 4,5-bis-(1,1,3,3-tetramethylbutyldithio)-1,2,3-thiadiazole.

Examples of the thiophosphate ester may include an alkyl trithiophosphite, an aryl or alkyl aryl thiophosphate, and a zinc dilauryldithiophosphate. Particularly, a lauryl trithiophosphite and a triphenyl thiophosphate are preferable.

The alkylthiocarbamoyl compound may be exemplified by a compound represented by the following formulae (6) and (7).

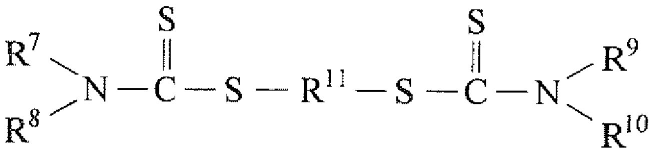
[0018]

[Chemical Formula 2]



$$\left.\begin{matrix}R^7\\R^8\end{matrix}\right\rangle N-\overset{\overset{S}{\|}}{C}-S-\overset{\overset{S}{\|}}{C}-N\left\langle\begin{matrix}R^9\\R^{10}\end{matrix}\right.$$

・・・・・・(6)



$$\left.\begin{matrix}R^7\\R^8\end{matrix}\right\rangle N-\overset{\overset{S}{\|}}{C}-S-R^{11}-S-\overset{\overset{S}{\|}}{C}-N\left\langle\begin{matrix}R^9\\R^{10}\end{matrix}\right.$$

・・・・・・(7)

[0019] In the formulae, R^7 to R^{10} each represent an alkyl group having 1 to 20 carbon atoms. R^{11} represents an alkylene group having 1 to 20 carbon atoms.
Examples of the alkylthiocarbamoyl compound may preferably include a bis(dimethylthiocarbamoyl)monosulfide, a bis (dibutylthiocarbamoyl)monosulfide, a bis(dimethylthiocarbamoyl)monosulfide, a bis(dibutylthiocarbamoyl)monosulfide, a bis(diamylthiocarbamoyl)monosulfide, a bis(dioctylthiocarbamoyl)monosulfide, and a methylene bis(dibutyldithiocarbamate).

[0020] The thiocarbamate compound may be exemplified by, for instance, a zinc dialkyldithiocarbamate. The thioterpene compound may be exemplified by, for instance, a reaction product of a phosphorus pentasulfide or pinene. The dialkyl thiodipropionate compound may be exemplified by, for instance, dilauryl thiodipropionate, or distearyl thiodipropionate.

[0021] By adding the sulfur compound as specified above in the lubricating oil composition, corrosion of engine parts can be considerably reduced.
However, the content of the above-described sulfur compound is 0.3 mass% or less in terms of sulfur contained in the -C-S-C-bond in the compound of the total amount of the composition. When the content of the sulfur contained in the -C-S-C-bond is 0.3 mass% or more, corrosion of the engine parts may be accelerated. The content of the sulfur is preferably 0.05 to 0.2 mass%.
Further, the sulfur compound preferably does not contain a -C-S_X-C-bond (x is an integer of 2 or more). In addition, a sulfur compound having a polysulfide structure is not preferable in light of corrosivity of engine parts. Especially, under the presence of the biofuel, an elution amount of copper and lead is increased.

[0022] The lubricating oil composition according to the invention preferably contains an alkaline earth metal-based detergent.
Examples of the alkaline earth metal-based detergent include alkaline earth metal sulfonate, alkaline earth metal phenate, alkaline earth metal salicylate and a mixture of two or more thereof.
Examples of the alkaline earth metal sulfonate include alkaline earth metal salt of alkyl aromatic sulfonic acid obtained by sulfonating an alkyl aromatic compound having a molecular weight of 300 to 1500 (preferably 400 to 700). The alkaline earth metal salt is exemplified by magnesium salt and/or calcium salt. Particularly, calcium salt is preferably used.
Examples of the alkaline earth metal phenate include alkaline earth metal salt of alkylphenol, alkylphenol sulfide and a Mannich reaction product of alkylphenol. The alkaline earth metal salt is exemplified by magnesium salt and/or calcium salt. Particularly, calcium salt is preferably used.
Examples of the alkaline earth metal salicylate include alkaline earth metal salt of alkyl salicylic acid, which is exemplified by magnesium salt and/or calcium salt. Particularly, calcium salt is preferably used. An alkyl group forming the alkaline earth metal-based detergent preferably has 4 to 30 carbon atoms. The alkyl group is more preferably a linear or branched alkyl group having 6 to 18 carbon atoms, in which 6 to 18 carbon atoms may be in a linear chain or in a branched chain. The alkyl group may be a primary alkyl group, a secondary alkyl group or a tertiary alkyl group.

[0023] In addition, the alkaline earth metal sulfonate, alkaline earth metal phenate and alkaline earth metal salicylate may be neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate and neutral alkaline earth metal salicylate obtained by: directly reacting the above-described alkyl aromatic sulfonic acid, alkylphenol, alkylphenol sulfide, a Mannich reaction product of alkylphenol, alkyl salicylic acid or the like with alkaline earth metal base exemplified by an oxide or a hydroxide of alkaline earth metal such as magnesium and/or calcium; or converting the above-described substance into alkali metal salt such as sodium salt or potassium salt and subsequently substituting the alkali metal salt with alkaline earth metal salt. Alternatively, the alkaline earth metal sulfonate, alkaline earth metal phenate and alkaline earth metal salicylate may be: basic alkaline earth metal sulfonate, basic alkaline earth metal phenate and basic alkaline earth metal salicylate obtained by heating neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate and neutral alkaline earth metal salicylate with excess alkaline earth metal salt or alkaline earth metal base under the presence of water; or overbased alkaline earth metal sulfonate, overbased alkaline earth metal phenate and overbased alkaline earth metal salicylate obtained by reacting neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate and neutral alkaline earth metal salicylate with carbonate or borate of alkaline earth metal under the presence of carbon dioxide gas.

[0024] The content of the alkaline earth metal-based detergent is preferably 0.35 mass% or less in terms of alkaline earth metal, more preferably 0.01 to 0.35 mass%, further more preferably 0.1 to 0.35 mass%. When the content of the alkaline earth metal-based detergent is 0.01 mass% or more, the lubricating oil composition exhibits more excellent oxidation stability, base-number retention and high-temperature detergency. On the other hand, when the content of the alkaline earth metal-based detergent exceeds 0.35 mass%, performance of catalyst for purifying exhaust gas may be deteriorated. In addition, when such is applied to a diesel engine with a DPF, an amount of ash content adhering to the DPF may be increased, thereby shortening the life of the DPF.

[0025] The lubricating oil composition according to the invention preferably contains a phenol-based antioxidant and/or an amine-based antioxidant as the antioxidant.

Examples of the phenol-based antioxidant are: octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; 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(2,5-di-t-butylphenol); 2,2'-methylenebis(4-methyl-6-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-4-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-octyl-3-(4-hydroxy-3,5-di-t-butylphenyl) propionate; n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate; and 2,2'-thio[diethyl-bis-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]. Among the above, a bisphenol-based antioxidant and an ester group-containing phenol-based antioxidant are preferable.

[0026] Examples of the amine-based antioxidant are: an antioxidant based on monoalkyldiphenylamine such as monooctyldiphenylamine and monononyldiphenylamine; an antioxidant based on dialkyl diphenylamine such as 4,4'-dibutyldiphenylamine, 4,4'-dipentyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine and 4,4'-dinonyldiphenylamine; an antioxidant based on polyalkyldiphenylamine such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine and tetranonyldiphenylamine; and an antioxidant based on naphthylamine, specifically alkyl-substituted phenyl-α-naphtylamine such as α-naphthylamine, phenyl-a-naphthylamine, butylphenyl-α-naphthylamine, pentylphenyl-α-naphthylamine, hexylphenyl-α-naphthylamine, heptylphenyl-α-naphthylamine, octylphenyl-α-naphthylamine and nonylphenyl-α-naphthylamine. Among the above, a dialkyl diphenylamine-based antioxidant and a naphthylamine-based antioxidant are preferable.

[0027] Incidentally, as another antioxidant, a molybdenum-amine complex-based antioxidant may be used. As the molybdenum-amine complex-based antioxidant, a hexahydric molybdenum compound, an example of which is a reaction product obtained by reacting molybdenum trioxide and/or molybdenum acid with an amine compound, may be used. The reaction product may be, for example, a compound obtained by the manufacturing method disclosed in JP-A-2003-252887. The amine compound to be reacted with the hexahydric molybdenum compound subjects to no particular limitation, and examples thereof are monoamine, diamine, polyamine and alkanolamine. Specific examples of the amine compound are: alkyl amine having an alkyl group of 1 to 30 carbon atoms (the alkyl group may contain a linear chain or a branched chain), exemplified by methylamine, ethylamine, dimethylamine, diethylamine, methylethylamine, methylpropylamine and the like; alkenyl amine having an alkenyl group of 2 to 30 carbon atoms (the alkenyl group may contain a linear chain or a branched chain), exemplified by ethenylamine, propenylamine, butenylamine, octenylamine and oleylamine; alkanol amine having an alkanol group of 1 to 30 carbon atoms (the alkanol group may contain a linear chain or a branched chain), exemplified by methanolamine, ethanolamine, methanolethanolamine and methanolpropanolamine; alkylenediamine having an alkylene group of 1 to 30 carbon atoms, exemplified by methylenediamine, ethylenediamine, propylenediamine and butylenediamine; polyamine such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine; a heterocyclic compound obtained by reacting monoamine, diamine and polyamine with a compound having an alkyl or alkenyl group of 8 to 20 carbon atoms or imidazoline, monoamine, diamine and polyamine being exemplified by undecyldiethylamine, undecyldiethanolamine, dodecyldipropanolamine, oleyldiethanolamine, oleylpropylenediamine and stearyltetraethylenepentamine; an alkylene-oxide adduct of the compounds; and a mixture thereof. In addition, sulfur-containing molybdenum complexes of succinimide as disclosed in JP-B-03-22438 and JP-A-2004-2866 may be used.

A mixing content of the antioxidant is preferably 0.3 mass% or more based on the total amount of the composition, more preferably 0.5 mass% or more. When the content exceeds 2 mass%, the antioxidant may not be dissolved in the base oil of the lubricating oil. Accordingly, the content of the antioxidant is preferably in a range from 0.3 to 2 mass% based on the total amount of the composition.

[0028] The lubricating oil composition according to the invention may be added as necessary with other additives such as a viscosity index improver, a pour point depressant, an antiwear agent, an ashless-type friction modifier, a rust inhibitor, a metal deactivator, a surfactant and an antifoaming agent as long as advantageous effects of the invention are not hampered.

[0029] Examples of the viscosity index improver are polymethacrylate, dispersed polymethacrylate, an olefin-based copolymer (such as an ethylene-propylene copolymer), a dispersed olefin-based copolymer, a styrene-based copolymer (such as a styrene-diene copolymer and a styrene-isoprene copolymer). In view of blending effects, a content of the viscosity index improver is 0.5 to 15 mass% based on the total amount of the composition, preferably 1 to 10 mass%.

[0030] Examples of the pour point depressant include polymethacrylate having a mass average molecular weight of 5000 to 50000.

Examples of the antiwear agent are: sulfur-containing compounds such as zinc dithiophosphate, zinc dithiocarbamate, zinc phosphate, disulfides, sulfurized olefins, sulfurized fats and oils, sulfurized esters, thiocarbonates, thiocarbamates (such as Mo-DTC) and the like; phosphorus-containing compounds such as phosphite esters, phosphate esters, phosphonate esters and amine salts or metal salts thereof; and a sulfur and phosphorus-containing antiwear agent such as thiophosphite esters, thiophosphate esters (such as Mo-DTP), thiophosphonate esters and amine salts or metal salts thereof. However, it should be noted that the antiwear agent as described above may accelerate corrosion of the engine parts when being used with the sulfur compound according to the invention.

[0031] Examples of the ashless-type friction modifier include a mono-type or bis-type polybutenyl succinimide and/or a boride thereof, a benzylamine, and a polyalkenylamine. The polybutenyl succinimide having a polybutenyl group having a mass average molecular weight of 700 to 3500 is preferable. Other examples of the ashless-type friction modifier are fatty acid, aliphatic alcohol, aliphatic ether, aliphatic ester, aliphatic amine and aliphatic amide, which have at least one alkyl or alkenyl group of 6 to 30 carbon atoms in the molecule.

An ashless dispersant is preferably added in a range from 0.5 to 10 parts by mass relative to 100 parts by mass of the base oil.

[0032] Examples of the rust inhibitor are petroleum sulfonate, alkylbenzene sulfonate, dinonylnaphthalene sulfonate, alkenyl succinic ester, multivalent alcohol ester. In view of blending effects, a content of the rust inhibitor is generally 0.01 to 1 mass% based on the total amount of the composition, preferably 0.05 to 0.5 mass%.

[0033] Examples of the metal deactivator (copper corrosion inhibitor) are benzotriazole-based compounds, tolyltriazole-based compounds, thiadiazole-based compounds, imidazole-based compounds, and pyrimidine-based compounds. Among the above, the benzotriazole-based compounds are preferable. By adding the metal deactivator, the engine parts can be prevented from being metallically corroded and degraded due to oxidation. Such a metal deactivator is preferably used with the sulfur compound as specified above.

In view of blending effects, a content of the metal deactivator is preferably 0.01 to 0.1 mass% based on the total amount of the composition, more preferably 0.03 to 0.05 mass%.

[0034] Examples of the surfactant are nonionic surfactants based on polyalkylene glycol such as polyoxyethylenealkylether, polyoxyethylenealkylphenylether and polyoxyethylenealkylnaphthylether.

[0035] Examples of the antifoaming agent are silicone oil, fluorosilicone oil, fluoroalkylether. In view of a balance between antifoaming effects and economic efficiecy, a content of the antifoaming agent is preferably approximately 0.005 to 0.1 mass% of the total amount of the compound.

[0036] Sulfur content of the lubricating oil composition according to the invention is preferably 0.5 mass% or less based on the total amount of the composition, more preferably 0.3 mass% or less, further more preferably 0.2 mass% or less. When the sulfur content is 0.5 mass% or less, deterioration of the catalyst performance for purifying exhaust gas can be effectively prevented.

Phosphorus content of the lubricating oil composition according to the invention is preferably 0.12 mass% or less based on the total amount of the composition, more preferably 0.1 mass% or less. When the phosphorus content is 0.12 mass% or less, deterioration of the catalyst performance for purifying exhaust gas can be effectively prevented.

[0037] Sulfate ash content of the lubricating oil composition according to the invention is preferably 1.1 mass% or less, more preferably 1 mass% or less. When the sulfate ash content is 1.1 mass% or less, deterioration of the catalyst performance for purifying exhaust gas can be effectively prevented. In addition, in a diesel engine, ash content accumulated on the filter of the DPF can be reduced, thereby preventing the filter blockage due to the ash and contributing to a long life of the DPF. The sulfate ash content means ash content obtained by adding sulfuric acid to carbonized residue caused by combustion of samples for heating so that the residue has a constant mass. The sulfate ash is generally used to know a rough amount of metal-based additives contained in the lubricating oil composition. Specifically, the sulfate ash is measured by a method prescribed in "5. Experiment Method of Sulfate Ash" of JIS K 2272.

Incidentally, when vaporizability of lubricating oil in an internal combustion engine is increased, more lubricating oil is consumed, which leads to a shortened lifetime of the lubricating oil. In addition, because more lubricating oil is dispersed within the exhaust gas catalyst, catalyst performance is lowered and catalyst lifetime is shortened. In view of the above, in the lubricating oil composition of the invention, NOACK evaporation measured according to JPI (abbreviation for Japan Petroleum Insititute, the same applies hereinafter)-5S-41-93 is preferably 15 mass% or less, more preferably 13 mass% or less, and further preferably 10 mass% or less.

[Examples]

[0038] Next, the invention will be further described in detail based on Examples, which by no means limit the invention.

[Examples 1 to 2 and Comparatives 1 to 4]

[0039] Lubricating oil compositions containing components shown in Table 1 respectively were prepared, which were then subjected to such a corrosivity test as follows. The components used for preparing the lubricating oil compositions were as follows.

(1) Base Oil : hydrorefining base oil; kinetic viscosity at 40 degrees C of 20.4 mm^2/s; kinetic viscosity at 100 degrees C of 4.28 mm^2/s; viscosity index of 116; %CA of 0.0; and sulfur content less than 20 ppm by mass
(2) Viscosity Index Improver: OCP; and mass average molecular weight of 800,000
(3) Pour Point Depressant: polyalkylmethacrylate; and mass average molecular weight of 60,000
(4) Metal-Based Detergent: overbased calcium salicylate; base number of 225 mg KOH/g (perchloric acid method); calcium content of 7.8 mass%; and sulfur content of 0.3 mass%
(5) Polybutenyl Succinic Monoimide A: number average molecular weight of a polybutenyl group being 1000; nitrogen content of 1.2 mass%; and boron content of 1.3 mass%
(6) Polybutenyl Succinic Bisimide B: number average molecular weight of the polybutenyl group being 2,000; nitrogen content of 1.2 mass%
(7) Phenol-Based Antioxidant: octadecyl-3-(3,5-tert-butyl-4-hydroxyphenyl)propionate.
(8) Amine-Based Antioxidant: dialkyl diphenylamine; and nitrogen content of 4.62 mass%
(9) Zinc Dialkyl Dithio Phosphate: Zn content of 9.0 mass%; phosphorus content of 8.2 mass%; sulfur content of 17.1 mass%; and the alkyl group being a mixture of a secondary butyl group and a secondary hexyl group
(10) Sulfuric Antioxidant A: methylene bis(dibutyldithiocarbamate).
(11) Sulfuric Antioxidant B: ditridecyl thiodipropionate.
(12) Sulfuric Antioxidant C: di-t-dodecyl trisulfide
(13) Sulfuric Antioxidant D: MoDTC
(14) Copper Corrosion Inhibitor: 1-[N,N-bis(2-ethylhexyl) aminomethyl] methyl benzotriazole.
(15) Antifoaming Agent: silicone antiforming agent

[0040] The measurement of properties of the lubricating oil compositions and the corrosivity test were conducted in the following manner.

(Calcium Content)

[0041] Measurement was conducted based on JPI-5S-38-92.

(Sulfur Content)

[0042] Measurement was conducted based on JIS K2541.

(Phosphorus Content)

[0043] Measurement was conducted based on JPI-5S-38-92.

(Sulfate Ash Content)

[0044] Measurement was conducted based on JIS K2272.

(Corrosivity Test)

[0045] As the lubricating oil composition to be tested, mixed oil in which biofuel (fuel obtained by transesterifying canola oil with methyl alcohol) was mixed by 10 mass% of each of the lubricating oil compositions (new oil) was used, assuming a mixing ratio of the fuel and the lubricating oil in an internal combustion engine.
In the corrosivity test, 100 g of the mixed oil was put as sample oil into a glass container (having a diameter of 40 mm and a height of 300 mm) and then air was blown into the glass container for 168 hours at 88 ml/min while the temperature of the oil is maintained at 125 degrees C. Subsequently, amounts of copper (Cu) and lead (Pb) eluted in the sample oil were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP).
In Reference Examples, the corrosivity test was also conducted using the lubricating oil composition that did not contain biofuel.
The properties of the lubricating oil compositions and the results of the corrosivity test are shown in Table 1.
[0046]

[Table 1]

		EXAMPLE 1	EXAMPLE 2	COMPARATIVE 1	COMPARATIVE 2	COMPARATIVE 3	COMPARATIVE 4	REFERENCE EXAMPLE 1	REFERENCE EXAMPLE 2
COMPOSITION (mass%)	BASE OIL	80.40	79.30	80.65	80.30	80.00	79.65	80.65	80.30
	VISCOSITY INDEX IMPROVER	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
	POUR POINT DEPRESSANT	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
	METAL-BASED DETERGENT	2.60	2.60	2.60	2.60	2.60	2.60	2.60	2.60
	POLYBUTENYL SUCCINIC MONOIMIDE A	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
	POLYBUTENYL SUCCINIC BISIMIDE B	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80
	PHENOL-BASED ANTIOXIDANT	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
	AMINE-BASED ANTIOXIDANT	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	ZINC DIALKYL DITHIO PHOSPHATE	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20

(continued)

		EXAMPLE 1	EXAMPLE 2	COMPARATIVE 1	COMPARATIVE 2	COMPARATIVE 3	COMPARATIVE 4	REFERENCE EXAMPLE 1	REFERENCE EXAMPLE 2
	SULFURIC ANTIOXIDANT A	0.25	0.00	0.00	0.00	0.00	1.00	0.00	0.00
	SULFURIC ANTIOXIDANT B	0.00	1.35	0.00	0.00	0.00	0.00	0.00	0.00
	SULFURIC ANTIOXIDANT C	0.00	0.00	0.00	0.35	0.00	0.00	0.00	0.35
	SULFURIC ANTIOXIDANT D	0.00	0.00	0.00	0.00	0.65	0.00	0.00	0.00
	COPPER CORROSION INHIBITOR	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
	ANTIFORMING AGENT	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
	TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(continued)

		EXAMPLE 1	EXAMPLE 2	COMPARATIVE 1	COMPARATIVE 2	COMPARATIVE 3	COMPARATIVE 4	REFERENCE EXAMPLE 1	REFERENCE EXAMPLE 2
CHARACTERISTICS OF COMPOSITION	CALCIUM CONTENT (mass%)	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
	SULFUR CONTENT (mass%)	0.35	0.33	0.25	0.33	0.31	0.65	0.25	0.33
	PHOSPHORUS CONTENT (mass%)	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
	SULFATE ASH CONTENT (mass%)	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
	SUF|LFUR CONTENT BASED ON -C-S-C-BOND (mass%)	0.10	0.08	0.00	0.08	0.06	0,04	0.00	0.08
CORROSIVITY TEST	Cu ELUTION AMOUNT (mass ppm)	6	6	11	31	68	300	8	6
	Pb ELUTION AMOUNT (mass ppm)	43	32	77	158	488	42	75	70

[Evaluation Results]

[0047] As is understood from the results of the corrosivity test shown in Table 1, Examples 1 and 2 in which the lubricating oil composition according to the invention was used produced a slight amount of copper (Cu) and lead (Pb) eluted in the oil even when the lubricating oil composition to which biofuel was added was used. Especially, it should be noted that the elution amount of lead was small as compared with that in the lubricating oil composition to which no biofuel was added as in Reference Examples 1 and 2.
On the other hand, when the specified sulfur compound of the invention was not mixed as in Comparative 1, the elution amounts of copper and lead were increased. In addition, even when the sulfur compound was mixed, the elution amounts of copper and lead were increased when the sulfur compound was polysulfide or the like as in Comparatives 2 and 3. Further, even when the specified sulfur compound was mixed, the elution amount of copper was increased when the amount of the sulfur compound was too large as in Comparative 4.

Industrial Applicability

[0048] This lubricating oil composition according to the present invention is favorably applied to an internal combustion engine in which biofuel or biofuel-mixed fuel is employed.

Claims

1. A lubricating oil composition used in an internal combustion engine, the internal combustion engine using a fuel that contains at least one fat and oil of natural fat and oil, hydrotreated natural fat and oil, transesterified natural fat and oil and hydrotreated transesterified natural fat and oil, wherein
a sulfur compound containing at least one -C-S-C-bond is added to base oil, and
a content of sulfur contained in the -C-S-C-bond is 0.3 mass% or less based on a total amount of the composition.

2. The lubricating oil composition according to claim 1, wherein the sulfur compound preferably does not contain a -C-S_X-C-bond
(where x is an integer of 2 or more).

3. The lubricating oil composition according to claim 1 or 2, further comprising an alkaline earth metal-based detergent in an amount of 0.35 mass% or less.

4. The lubricating oil composition according to any one of claims 1 to 3, further comprising a phosphorus in an amount of 0.12 mass% or less based on the amount of the composition.

5. The lubricating oil composition according to any one of claims 1 to 4, further comprising a sulfate ash in an amount of 1.1 mass% or less.

6. The lubricating oil composition according to any one of claims 1 to 5, further comprising at least one of a phenol-based antioxidant and an amine-based antioxidant in an amount of 0.3 mass% or more based on the total amount of the composition.

7. The lubricant oil composition according to any one of claims 1 to 6, further comprising a sulfur in an amount of 0.5 mass% or less based on the total amount of the composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/052219

A. CLASSIFICATION OF SUBJECT MATTER
C10M135/00(2006.01)i, *C10M129/10*(2006.01)i, *C10M133/12*(2006.01)i, *C10M135/18*(2006.01)i, *C10M135/22*(2006.01)i, *C10M159/22*(2006.01)i, *C10M159/24*(2006.01)i, *C10M169/04*(2006.01)i, *C10N10/04*(2006.01)n, *C10N30/12*(2006.01)n,
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M135/00, C10M129/10, C10M133/12, C10M135/18, C10M135/22, C10M159/22, C10M159/24, C10M169/04, C10N10/04, C10N30/12, C10N40/25

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	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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.
A	JP 2007-520618 A (Chemtura Corp.), 26 July, 2007 (26.07.07), Claims; Par. Nos. [0001] to [0002], [0005] to [0007], [0017] to [0021], [0030]; examples & WO 2005/078054 A1 & EP 1713891 A1 & US 2005/0170978 A1	1-7
A	JP 2000-1684 A (Oronite Japan Ltd.), 07 January, 2000 (07.01.00), Claims; Par. Nos. [0002], [0010] to [0012], [0016], [0022] to [0029], [0041]; trially manufactured product No.5 of engine oil & EP 0528610 A1 & JP 6-41568 A & US 2002/0098990 A1	1-7

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

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 07 May, 2009 (07.05.09)	Date of mailing of the international search report 19 May, 2009 (19.05.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/052219

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AGARWAL A K, Experimental investigations of the effect of biodiesel utilization on lubricating oil tribology in diesel engines, Proceedings of the Institution of Mechanical Engineers Part D, 2005.05, Vol.219 No.D5, p.703-713	1-7
A	WO 2005/090532 A1 (Nippon Oil Corp.), 29 September, 2005 (29.09.05), Par. No. [0030]; examples 1 to 2, 4 to 7 & EP 1736529 A1 & JP 2005-264066 A & US 2007/0179070 A1	1-7
A	WO 2007/119299 A1 (Nippon Oil Corp.), 25 October, 2007 (25.10.07), Page 36, lines 10 to 17; line 23 to page 37, line 8 & EP 1997871 A1 & JP 2007-254559 A	1-7

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/52219

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

C10N40/25(2006.01)n

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

Form PCT/ISA/210 (extra sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2003252887 A **[0027]**
- JP 3022438 B **[0027]**
- JP 2004002866 A **[0027]**

Non-patent literature cited in the description

- **Koji YAMANE.** *BIODIESEL- From Deep Fryer to Fuel Tank,* May 2006 **[0003]**