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(54) Title: LUBRICATING OIL COMPOSITION FOR DIESEL ENGINES

(57) Abstract: The invention provides a lubricating oil composition for diesel engines which contains a GTL base oil with a kinematic viscosity at 100°C of 4.5 to 5.5 mm²/s, a comblike PMA (polymethacrylate) based viscosity index improver and a boron-containing dispersant and/or boron-containing detergent, the total content of the boron-containing dispersant and/or boron-containing detergent in terms of conversion to boron content relative to the total amount of the composition being not less than 0.025 mass%, and which satisfies 0W-30 or 5W-30 in the SAE J300 standard.



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LUBRICATING OIL COMPOSITION FOR DIESEL ENGINES

Field of the Invention

This invention relates to an engine oil for automobiles (lubricating oil composition for internal combustion engines), and more specifically relates to a lubricating oil composition for diesel engines with superior fuel efficiency, oil consumption control and detergency.

Background of the Invention

One problem with crankcase lubricating oils is that the lubricating oil is liable to escape from the crankcase because of so-called blow-by gas. The blow-by gas, or gas/lubricating oil mixtures of this kind, are preferably recycled in the engine rather than being exhausted to the atmosphere. In some engines such recycling is carried out by injecting the blow-by gas into the engine's air-intake system so that the lubricating oil is combusted in the piston chambers. Recycling of the blow-by gas solves the problem of emissions but, on the other hand, there is the possibility that problems may arise in that deposits may form in the air-intake system. For example, if the deposits form in the air compressor, the compressor will not work properly and will even be prone to damage. As a further example, if an air cooler is present between the compressor and the cylinder block crankcase, the air cooler may become contaminated. There has been a demand for the provision of diesel engine systems that will prevent or reduce the formation of such deposits, see for example JP5501620.

At the same time, there has been a demand for lower

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fuel consumption. To achieve lower fuel consumption investigations have been carried out to manufacture compositions having the appropriate viscosity characteristics by using friction modifiers to contribute to friction reducing performance, and by using viscosity index improvers to bring about a reduction in churning resistance and to maintain an oil film at high temperatures while having low viscosity at low temperatures, as described in Japanese Laid-open Patent 2014-210844.

However, there has been nothing yet which achieves enough satisfaction in suppressing deposit formation, demonstrating fuel economy and maintaining performance over long periods. Also, it seems that in future the downsizing of commercial vehicles which are fitted with diesel engines by adding boosting devices will keep on advancing, and it may be expected that the thermal loads on engine oils will increase. However, there has been the problem that good volatility has not been achieved with the lubricating oil compositions of the prior art.

The purpose of this invention, therefore, is to offer a lubricating oil composition for use in diesel engines which, when used as an engine oil for vehicles, does have excellent volatility and engine cleaning properties as well as fuel economising performance.

Summary of the Invention

By dint of intensive research, the inventors have discovered that it is possible to solve the aforementioned problems by blending a specified base oil and a specified viscosity index improver with a specified dispersant and detergent and thereby satisfying the specified viscosity grade, and have thus perfected this invention. Specifically the invention is as follows.

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Aspect (I) of the invention is a lubricating oil composition for diesel engines characterised in that it contains:

- 5 a) a GTL base oil with a kinematic viscosity at 100°C of 4.5 to 5.5 mm²/s,
 - b) a comb-like PMA (polymethacrylate) based viscosity index improver and
 - 10 c) not less than 0.025 mass% of a boron-containing dispersant and/or boron-containing detergent in terms of conversion to boron content (total amount) relative to the total amount of the composition,
- wherein it satisfies 0W-30 or 5W-30 in the SAE J300 standard.

Aspect (II) of the invention is a lubricating oil composition for diesel engines in accordance with Aspect (I) which also includes a non-comb-like PMA (polymethacrylate) based viscosity index improver and an SCP (styrene-diene copolymer) based viscosity index improver and/or an OCP (olefin copolymer) based viscosity index improver and which further satisfies at least one of the following (1) to (3), the polymer amounts being minus diluents.

(1) Non-comb-like PMA based viscosity index improver content/total viscosity index improver content (polymer having weight-average molecular weight of not less than 50,000): not more than 0.7

(2) OCP based viscosity index improver content/total viscosity index improver content (polymer having weight-average molecular weight of not less than 50,000): not more than 0.2

(3) SCP based viscosity index improver content/total viscosity index improver content (polymer having weight-average molecular weight of not less than 50,000): not

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more than 0.3

Aspect (III) of the invention is a lubricating oil composition for diesel engines in accordance with Aspect (I) or (II) satisfying the following viscosity characteristic.

$$\frac{[HTHS\ 100^{\circ}C\ viscosity\ (capillary\ method) - HTHS\ 100^{\circ}C\ viscosity\ (TBS\ method)]}{HTHS\ 100^{\circ}C\ viscosity\ (TBS\ method)} = 0.07\ to\ 0.15$$

According to this invention, it is possible to offer a lubricating oil composition for use in diesel engines which, when used as an engine oil for vehicles, has excellent volatility and engine cleaning properties as well as fuel economising performance.

Detailed Description of the Invention

The constituents (constituent elements), composition (contents of each constituent) and physical characteristics of the lubricating oil composition for diesel engines relating to this invention are described below, but the invention is in no way limited by these.

The lubricating oil composition of the present embodiment contains a GTL base oil as the base oil, a comb-like PMA based viscosity index improver and a boron-containing dispersant and/or boron-containing detergent, and other constituents where necessary.

GTL (gas-to-liquid) oils synthesised by the Fischer-Tropsch process in the technology for liquefying fuels from natural gas are used as the base oil for the lubricating oil composition of this invention. Using such base oils makes it possible, in the framework of this invention, to improve oxidative stability as well as reducing evaporative losses.

When using comb-like polymers, in comparison with Yubase base oils it is possible to improve fuel consumption by using GTL base oils because, especially

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within the framework of this invention, the temporary shear viscosity at 100°C falls.

In particular, in this invention a GTL base oil having a kinematic viscosity at 100°C of 4.5 to 5.5 mm²/s is used. If the kinematic viscosity at 100°C of the base oil falls below 4.5, satisfactory volatility is not obtained. If the kinematic viscosity at 100°C exceeds 5.5, satisfactory fuel economy is not obtained.

Here, in order to obtain a base oil where the kinematic viscosity at 100°C is 4.5 to 5.5 mm²/s, it is preferable if it is a single GTL base oil with a kinematic viscosity at 100°C of 4.5 to 5.5 mm²/s, but in the case of manufacture it is suitable to mix two kinds, a GTL base oil (a1) where the kinematic viscosity at 100°C is 3.0 to 6.0 mm²/s and a GTL base oil (a2) where the kinematic viscosity at 100°C is 7.0 to 13 mm²/s. If the kinematic viscosity at 100°C of the low viscosity base oil constituent (a1) is below 3.0 mm²/s, the amount of evaporation increases, and it becomes difficult to maintain the viscosity of the composition over long periods. If using a high viscosity base oil constituent (a2) where the kinematic viscosity at 100°C exceeds 13 mm²/s, the low temperature viscosity at -40°C increases and low-temperature startability worsens. Furthermore, in this case, the ideal viscosity index of the mixed GTL base oil is 120 to 180, but 120 to 150 is even better.

For these GTL base oils a total sulphur content of less than 10 ppm is typically ideal, and a total nitrogen content of less than 1 ppm is even better. One example of such a GTL base oil product is Shell XHVI (trade name).

The lubricating oil of the present embodiment may also include a boron-containing detergent as a detergent. There are no special restrictions for the boron-

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containing detergent, but mention may be made of boron-containing alkaline earth metal salts. More specifically, mention may be made of borated alkaline earth metal alkylsalicylate detergents and borated alkaline earth metal alkyl toluene sulphonate detergents. Borated calcium alkyltoluene sulphonate is ideal. Instances in the known art may be used for such boron-containing detergents (for example, borated alkaline earth metal alkyl toluene sulphonate detergents may be manufactured in accordance with Japanese Laid-open Patent 2008-297547).

The lubricating oil composition of the present embodiment here may also include other detergents (for example, metallic detergents) so long as the effect of the invention is not impeded. As examples of metallic detergents, mention may be made of alkaline earth metal sulphonates, alkaline earth metal phenates, alkaline earth metal salicylates and alkaline earth metal naphthenates. As examples of the alkaline earth metals, mention may be made of calcium and magnesium. These may be used singly or in combinations of two or more kinds. Normally, use of sulphonates, phenates and salicylates of calcium or magnesium is preferred. For alkaline earth metal phenates it is preferable to use alkaline earth metal salts, especially calcium salts, of alkylphenols, alkylphenol sulphides and alkylphenol Mannich reaction products having straight-chain or branched alkyl groups of carbon number 4 to 30, but preferably 6 to 18. For alkaline earth metal salicylates it is preferable to use alkaline earth metals salts, and with special preference magnesium salts and/or calcium salts, of alkyl salicylic acids having straight-chain or branched alkyl groups of carbon number 1 to 30, but preferably 6 to 18. The base

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numbers of these may be freely chosen according to the type and purpose of the corresponding lubricating oil.

The lubricating oil composition of the present embodiment may include a boron-containing dispersant as a
5 dispersant. For example, polybutenyl succinimide based dispersants, polybutenyl succinamide based dispersants, benzylamine based dispersants and succinate ester based dispersants may be borated.

Polybutenyl succinimides are obtained from
10 polybutenes obtained by polymerisation of high-purity isobutene or mixtures of 1-butene and isobutene using a fluorinated boron based catalyst or an aluminium chloride based catalyst, and the products having a vinylidene structure at the terminals are normally contained in the
15 amount of 5 to 100 mol%. From the standpoint of sludge-inhibiting effects, it is preferable to include 2 to 5, and in particular 3 to 4, nitrogen atoms in the polyalkylene-polyamine chains. Also, as polybutenyl succinimide derivatives, it is possible to use the so-
20 called modified succinimides in which some or all of the amino and/or imino groups present have been neutralised or amidified by making boric acid compounds or oxygen-containing organic compounds such as alcohols, aldehydes, ketones, alkylphenols, cyclic carbonates and organic
25 acids act on the aforementioned polybutenyl succinimide compounds.

The lubricating oil composition of the present embodiment may be such as to contain any and at least one of the above mentioned boron-containing detergents and
30 boron-containing dispersants, and any such forms that contain boron-containing detergents only, boron-containing dispersants only, or boron-containing detergents and boron-containing dispersants together are

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within the scope of this invention.

As examples of anti-wear agents imparting wear resistance and extreme-pressure resistance that can be used in the lubricating oil composition of the present embodiment, mention may be made of zinc dithiophosphates (ZnDTP). Typical examples of ZnDTP generally include zinc dialkyldithiophosphates, zinc diaryldithiophosphates and zinc arylalkyldithiophosphates. The alkyl groups here may be straight-chain or branched. For example, as regards the alkyl groups of the zinc dialkyldithiophosphates, zinc dialkyldithiophosphates having primary or secondary alkyl groups of carbon number 3 to 22 or alkylaryl groups substituted with alkyl groups of carbon number 3 to 18 may be used. As specific examples of zinc dialkyldithiophosphates, mention may be made of zinc dipropyldithiophosphate, zinc dibutyldithiophosphate, zinc dipentyldithiophosphate, zinc dihexyldithiophosphate, zinc diisopentyldithiophosphate, zinc diethylhexyldithiophosphate, zinc dioctyldithiophosphate, zinc dinonyldithiophosphate, zinc didecyldithiophosphate, zinc didodecyldithiophosphate, zinc dipropylphenyldithiophosphate, zinc dipentylphenyldithiophosphate, zinc dipropylmethylphenyldithiophosphate, zinc dinonylphenyldithiophosphate, zinc didodecylphenyldithiophosphate and zinc didodecylphenyl dithiophosphate.

The metal deactivators that can be used in the lubricating oil composition of the present embodiment include benzotriazoles and benzotriazole derivatives such as alkyl-tolyltriazoles, and benzimidazoles and benzimidazole derivatives such as tolimidazoles. Further

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examples are indazole derivatives such as tolylindazoles, benzothiazoles and benzothiazole derivatives such as tolylthiazoles. Mention may also be made of benzoxazole derivatives, thiadiazole derivatives and tolazole derivatives.

5 Examples of the anti-oxidants used in the lubricating oil composition of the present embodiment include amine-based anti-oxidants and phenol-based anti-oxidants. As examples of the aforementioned amine-based anti-oxidants, mention may be made of dialkyl-
10 diphenylamines such as p,p'-dioctyl-diphenylamine (Nonflex OD-3, made by Seiko Chemical Ltd), p,p'-di- α -methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-
15 butyldiphenylamine and monooctyldiphenylamine, bis(dialkylphenyl)amines such as di(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octyl-phenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine, 1-
20 naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine,
25 and phenothiazines such as Phenothiazine (made by Hodogaya Chemical Ltd.) and 3,7-dioctylphenothiazine. Phenol-based anti-oxidants include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-
30 butylhydroquinone (Antage DBH, made by Kawaguchi Chemical Industry Co. Ltd.), 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butyl-4-methylphenol and

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2,6-di-t-butyl-4-ethylphenol, and 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol. Also, there are 3,5-di-t-butyl-4-hydroxybenzylmercapto-octylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate (Yoshinox SS, made by Yoshitomi Fine Chemicals Ltd.), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, and benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-C7~C9 side-chain alkyl ester (Irganox L135, made by Ciba Specialty Chemicals Ltd.), 2,6-di-t-butyl- α -dimethylamino-p-cresol, and 2,2'-methylenebis(4-alkyl-6-t-butylphenol)s such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (Antage W-400, made by Kawaguchi Chemical Industry Ltd.) and 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (Antage W-500, made by Kawaguchi Chemical Industry Ltd). Furthermore, there are bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (Antage W-300, made by Kawaguchi Chemical Industry Ltd.), 4,4'-methylenebis(2,6-di-t-butylphenol) (Ionox 220AH, made by Shell Japan Ltd.), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A, made by Shell Japan Ltd.), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethylene glycol bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (Irganox L109, made by Ciba Specialty Chemicals Ltd.), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (Tominox 917, made by Yoshitomi Fine Chemicals Ltd.), 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (Irganox L115, made by Ciba Specialty Chemicals Ltd.), 3,9-bis{1,1-dimethyl-2-

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[3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy]ethyl} 2,4,8,10-tetraoxaspiro[5,5]undecane (Sumilizer GA80, made by Sumitomo Chemicals), 4,4'-thiobis(3-methyl-6-t-butylphenol) (Antage RC, made by Kawaguchi Chemical Industry Ltd.) and 2,2'-thiobis(4,6-di-t-butyl-resorcinol). Mention may also be made of polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]methane (Irganox L101, made by Ciba Specialty Chemicals Ltd.), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (Yoshinox 930, made by Yoshitomi Fine Chemicals Ltd.), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (Ionox 330, made by Shell Japan Ltd.), bis-[3,3'-bis-(4'-hydroxy-3'-t-butylphenyl) butyric acid] glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl) methyl-4-(2'',4''-di-t-butyl-3''-hydroxyphenyl)methyl-6-t-butylphenol and 2,6,-bis(2'-hydroxy-3'-t-butyl-5'-methyl-benzyl)-4-methylphenol, and phenol-aldehyde condensates such as condensates of p-t-butylphenol and formaldehyde and condensates of p-t-butylphenol and acetaldehyde.

The lubricating oil composition of the present embodiment includes a comb-like polymethacrylate-based viscosity index improver. What is meant by a comb-like polymer is a polymer having a plurality of extended side chains in a comb form relative to the main polymer chain. The viscosity index improvers of the present embodiment include, among these comb-like polymers, viscosity index improvers which are comb-like polymethacrylate-based polymers. In this invention, what is meant by a "viscosity index improver" denotes a polymer having a weight average molecular weight of not less than 50,000.

Suitable instances of the comb-like polymethacrylate-based viscosity index improvers that may

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be used in the present embodiment are, for example, the polymers disclosed in Japanese Laid-open Patent 2010-532805.

Also, the comb-like polymethacrylate-based viscosity index improvers of the present embodiment ideally have a weight average molecular weight of 200,000 to 600,000, those of 250,000 to 500,000 are even better, and those of 300,00 to 450,000 are best of all. The PSSI (permanent shear stability index) is ideally not more than 10.

As specific examples of such comb-like polymethacrylate-based viscosity index improvers, mention may be made of Viscoplex 3-201 (registered trade mark) and Viscoplex 3-220 (registered trade mark).

The lubricating oil composition of the present embodiment may include viscosity index improvers other than comb-like polymethacrylate-based viscosity index improvers. As examples of such viscosity index improvers, mention may be made of one kind or more of polymers selected from the group comprising non-comb-like PMA (polymethacrylates), OCP (olefin copolymers) and SCP (styrene-diene copolymers).

For non-comb-like PMA (polymethacrylate)-based viscosity index improvers it is possible to use without any special restriction those known in the art, but those having a weight average molecular weight of 100,000 to 400,000 are ideal. Specific examples of such a PMA are those disclosed in Japanese Laid-open Patent 2014-125569.

For OCP (olefin copolymer)-based viscosity index improvers it is possible to use without any special restriction those known in the art, but those having a weight average molecular weight of 50,000 to 300,000 are ideal. Specific examples of such an OCP are those disclosed in Japanese Laid-open Patent 2014-125569.

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For SCP (styrene-diene copolymer)-based viscosity index improvers it is possible to use without any special restriction those known in the art, but those having a weight average molecular weight of 200,000 to 1,000,000 are ideal. A specific example of such an SCP is Infineum (registered trade mark) SV150.

The lubricating oil composition of the present embodiment may contain polymers other than comb-like polymethacrylates as viscosity index improvers.

Such viscosity index improvers (polymers having a weight average molecular weight of not less than 50,000) are in general blended in a diluted state in a suitable liquid medium to make them easier to handle.

As examples of the defoamers that can be used in the lubricating oil composition of the present embodiment, mention may be made of organosilicates such as dimethylpolysiloxane, diethyl silicate and fluorosilicones and non-silicone based defoamers such as polyalkylacrylates.

The base oil content is ideally 60 to 90 mass% in terms of the total mass of the lubricating oil composition, but 65 to 90 mass% is better, and the range 70 to 85 mass% is better yet.

The content of viscosity index improvers (amount of viscosity index improvers as a whole) is not specially restricted and may be modified as appropriate. For example it may be 0.05 to 20 mass% in terms of the total mass of the lubricating oil composition. The ideal amounts of each of the various viscosity index improvers are given below.

There is no special restriction on the content of the comb-like PMA, but ideally it is 1.0 to 6.0 mass% in terms of the total amount of the lubricating oil

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composition, but 1.0 to 5.0 mass% is better and 1.0 to 4.0 mass% is best of all.

The non-comb-like PMA content is ideally such that non-comb-like PMA content / total viscosity index improver content is not more than 0.7.

The OCP content is ideally such that OCP content / total viscosity index improver content is not more than 0.2.

The SCP content is ideally such that SCP content / total viscosity index improver content is not more than 0.3.

If non-comb-like PMA (polymethacrylates), SCP (styrene-diene copolymers) and OCP (olefin copolymers) are included as viscosity index improvers, and these satisfy at least one (but ideally all) of the aforementioned ranges, it is possible within the framework of this invention to achieve the effects of the invention and also to reduce manufacturing costs.

In order to obtain the desired effect, the content of the boron-containing detergent and/or boron-containing dispersant must be not less than 0.025 mass% in terms of the boron content conversion value (total amount). The upper limit is not specially restricted, but may for example be not more than 0.1 mass% (ideally not more than of the order of 0.050 mass%).

An explanation will be given of the ideal added amounts for other constituents which may be added to the lubricating oil composition of the present embodiment. First, the ideal added amount of anti-oxidants, individually or in combinations of plural kinds, will be in the range 0.01 to 2 mass% in terms of the total mass of the lubricating oil composition. The ideal added amount of metal deactivators, individually or in

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combinations of plural kinds, will be in the range 0.01 to 0.5 mass% in terms of the total mass of the lubricating oil composition. The ideal added amount of anti-wear agents (for example ZnDTP), individually or in combinations of plural kinds, will be, for example, in the range, as amount of phosphorus (P), 0.01 to 0.10 mass% but more preferably 0.05 to 0.08 mass% in terms of the total mass of the lubricating oil composition. The ideal added amount of defoamers, individually or in combinations of plural kinds, will be, for example, 0.0001 to 0.01 mass% in terms of the total mass of the lubricating composition. The ideal added amount of metallic detergents, individually or in combinations of plural kinds, will be, for example, 0.05 to 0.3 mass%, but more preferably 0.1 to 0.2 mass%, in terms of the total mass of the lubricating composition. The ideal added amount of ashless dispersants, individually or in combinations of plural kinds, will be, for example, be such as to present of the order of 0.01 to 0.3 mass% of nitrogen in terms of the total mass of the lubricating composition.

It is considered here that there is an excellent correlation between HTHS viscosity at 100°C and fuel consumption characteristics. There are various methods of measuring HTHS viscosity. Among them, there are cases where the viscosity obtained by measuring the HTHS viscosity by the capillary method and the viscosity measured by the TBS method differ, depending on the type of viscosity index improver used. Given that, to the extent that the value in Formula (1) below is large, the viscosity component as measured by the method using a capillary tube type viscometer (the capillary method) will be large, and the viscosity component as measured by

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using a rotational viscometer (TBS method) will be small, revealing that the difference between them will increase. In those cases, it denotes that the shear viscosity of the oil becomes smaller at sliding friction positions in situations close to such rotational viscometers between the crankshaft bearings. In other words, it is considered that it is possible to reduce the viscous resistance and to reduce the friction losses at the aforementioned positions. At the same time, at positions where the oil is subject to shear in situations close to a capillary viscometer, it is possible to maintain a high shear viscosity and thus satisfactory durability.

With the lubricating oil composition of the present embodiment, it was discovered that $[(\text{capillary viscosity} - \text{TBS viscosity}) / \text{TBS viscosity}]$ satisfies 0.07 to 0.15, and in that connection low fuel consumption was manifested.

The method of measuring the capillary viscosity here is the value measured in accordance with the ASTM D5481 test method (150°C), taking the temperature condition at 100°C (shear velocity $1.0 \times 10^6 \text{S}^{-1}$).

The method of measuring the TBS viscosity is the value measured by means of the method described in Japanese Patent 5565999.

Examples

The invention is further explained next by means of examples of embodiment and comparative examples, but the invention is in no way limited by these examples.

The raw materials used in the examples of embodiment were as follows. The characteristics of the various base oils are shown in Table 1.

Base Oils

- Base oil 1: XHVI 4 (GTL oil)

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- Base oil 2: XHVI 8 (GTL oil)
- Base oil 3: XHVI 3 (GTL oil)
- Base oil 4: Yubase 4 (mineral oil)
- Base oil 5: Yubase 8 (mineral oil)
- 5 • Base oil 6: Yubase 3 (mineral oil)

Additives Packages

DH-2 DI package 1: As shown in the tables, in the examples of embodiment when 14.00% was added, the boron content of the lubricating oil became 0.033 mass%
10 {including boron-containing dispersant (borated calcium alkyltoluene sulphonate) and boron-containing detergent (borated succinate ester-based dispersant), and amount of other additives same as DI packages 2 and 3}

DH-2 DI package 2: As shown in the tables, in the
15 examples of embodiment when 14.00% was added, the boron content of the lubricating oil became 0.027 mass%
{including boron-containing dispersant (borated calcium alkyltoluene sulphonate) and boron-containing detergent (borated succinate ester-based dispersant), and amount of
20 other additives same as DI packages 1 and 3}

DH-2 DI package 3: As shown in the tables, in the examples of embodiment when 14.00% was added, the boron content of the lubricating oil became 0.020 mass%
25 {including boron-containing dispersant (borated calcium alkyltoluene sulphonate) and boron-containing detergent (borated succinate ester-based dispersant), and amount of other additives same as DI packages 1 and 2}

Viscosity Index Improvers

- Viscosity index improver solution 1: Solution
30 containing Viscoplex 3-220 (comb-like PMA-based viscosity index improver) (approx. 40% dilution)
- Viscosity index improver solution 2: Solution containing Viscoplex 3-201 (comb-like PMA-based viscosity

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index improver) (approx. 60% dilution)

- Viscosity index improver solution 3: Solution containing Viscoplex 6-954 (non-comb-like PMA-based viscosity index improver) (approx. 40% dilution)
- 5 • Viscosity index improver solution 4: Solution containing Lz7177B (olefin copolymer -based viscosity index improver) (approx. 87.5% dilution)
- Viscosity index improver solution 5: Solution containing Infineum (registered trade mark) SV150
10 (styrene-diene copolymer-based viscosity index improver) (approx. 93.5% dilution)

Defoamer

- DCF 3 mass% solution

Table 1

Base oil name	Base oil 1	Base oil 2	Base oil 3	Base oil 4	Base oil 5	Base oil 6
API category	Group 3	Group 3	Group 2	Group 3	Group 3	Group 2
Kinematic viscosity						
@ 100°C mm ² /s	4.1	7.6	2.7	4.2	7.6	3.1
@ 40°C mm ² /s	17.9	43.7	9.9	19.3	46.6	12.4
Viscosity index JIS K 2283	130	143	112	125	129	10.4
Noack evaporative loss mass% ASTM D5800	13.2	4.6	42.5	14.8	5.6	44
Ring analysis ASTM D3238						
%CA	0	0	0	0	0	0
%CN	7.9	12	9.2	21.8	22.9	31.2
%CP	92.1	88	90.8	78.2	77.1	68.8
Sulphur content mass% ASTM D2622	<0.01	<0.01	3.3	2.75	4	2.5
Flash point (CCC) °C JIS K2265-4	220	3.45	204	220	256	194
Pour point °C JIS K 2269	-37.5	3.8	-37.5	2.1	-12.5	-32.5

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The aforementioned raw materials were blended as shown in Tables 2 and 3, and the lubricating oil compositions of Examples of Embodiment 1 to 8 and Comparative Examples 1 to 10 were obtained.

5 Evaluation

Next, evaluation tests were carried out in respect of the lubricating oil compositions of Examples of Embodiment 1 to 8 and Comparative Examples 1 to 10. It was confirmed that all the lubricating oil compositions for Examples of Embodiment 1 to 8 satisfied 5W-30.

10 An evaluation of the fuel consumption characteristics was carried out on the basis of fuel consumption bench tests using a 4000 cc diesel engine of Japanese make. The operating conditions were set up with reference to the Ministry of Land, Infrastructure and Transport 10•15 mode. The gallery temperature at measurement time was set at 90°C. The results shown in Tables 2 and 3 show the rate of improvement (%) in fuel economy when taking as a criterion a commercial diesel engine oil classified as SAE viscosity grade 10W-30. In the evaluation, if the rate of improvement (%) in fuel economy was at least 1.0, the fuel consumption characteristics were marked O (good).

25 The Noack volatility (%) was measured on the basis of ASTM D5800. For the evaluation, if the Noack volatility (%) was not more than 13.0, volatility was marked O (good).

30 Hot tube tests were carried out in accordance with the Japan Petroleum Institute's standard JPI-5S-55-99 "Engine oils - Hot tube test." The test conditions were set at a test temperature of 290°C/300°C, test duration 16 hours, sample oil feed rate of 0.3 ml/hour and air flow of 10 ml/hour, and if the evaluation (merit points)

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of the colour of discoloured portion of the glass tube after completion of the test was at least 7.0, detergency was marked O (good).

5 The [capillary viscosity - TBS viscosity) / TBS viscosity] was calculated by following the aforementioned method.

10 In addition, the (40°C) kinematic viscosity, (100°C) kinematic viscosity, viscosity index (VI), boron content (total value), calcium content (total value), phosphorus content (total value), zinc content (total value), nitrogen content (total value) and molybdenum content (total value) were calculated (the base stock Vk 100°C was the 100°C kinematic viscosity of the base oil mixture).

Fuel economy improvement ratio 60°C (%)	0	0	0	0	0	0	0	0	0	0	0
Volatility NOACK	0	0	0	0	0	0	0	0	0	0	0
Detergency HTT (300°C)	0	0	0	0	0	0	0	0	0	0	0
Vk40 mm ² /s	42.23	42.42	49.46	49.24	46.89	45.73	49.51	42.24	42.24	42.24	42.24
Vk100 mm ² /s	10.43	11.00	10.46	10.51	10.45	10.34	10.24	10.45	10.45	10.45	10.45
VI	248	264	208	210	221	224	201	248	248	248	248
Base stock Vk 100°C mm ² /s	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
(HTHS (capillary, 100°C) - HTHS (TBS, 100°C) / HTHS (TBS, 100°C)	0.10	0.11	0.09	0.08	0.08	0.10	0.09	0.10	0.10	0.10	0.10
B mass%	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.033
Ca mass%	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220
P mass%	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096
Zn mass%	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110
N mass%	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120
Mo mass%	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Fuel efficiency test, oil temp. 60°C											
FE improvement ratio against	1.5	1.5	1.4	1.0	1.3	1.3	1.1	1.5	1.5	1.5	1.5

Table 3 - Comparative Examples

Comparative Example	1	2	3	4	5	6	7	8	9	10
Base oil 1		57.60	57.60	57.60	57.60	24.80	79.36			57.60
Base oil 2	84.43	28.37	28.37	28.37	28.37	57.87				28.37
Base oil 3								76.47		
Base oil 4									63.39	
Base oil 5									17.88	
DH2 DI package 1	14.00	14.00	14.00	14.00	14.00	14.00	14.00	14.00	14.00	
DH2 DI package 2										
DH2 DI package 3										14.00
VI imp. solution 1 (comb-like PMA)	1.54 (0.92)					3.3 (1.96)	6.61 (3.97)	9.5 (5.70)	4.7 (2.82)	5.5 (3.30)
VI imp. solution 2 (comb-like PMA)										
VI imp. solution 3 (non-comb-like PMA)		5.1 (3.10)		3.8 (2.28)						
VI imp. solution 4 (olefin copolymer)			7.6 (0.95)	2.3 (0.29)						
VI imp.					18.5					

solution 5 (styrene-diene copolymer)								(1.20)							
Defoamer	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Fuel economy characteristics															
FE improvement ratio 60°C (%)	X	X	X	X	X	X	X	X	O	O	O	O	O	O	O
Volatility NOACK	O	O	O	O	O	O	O	O	O	X	X	X	X	O	O
Detergency HTT (300°C)	O	O	O	O	O	O	O	O	O	O	O	O	O	X	X
Vk40 mm²/s	61.49	51.91	58.97	53.70	58.35	52.85	38.52	33.41	44.28	42.30					
Vk100 mm²/s	10.48	10.49	10.42	10.53	10.56	10.49	10.51	10.71	10.48	10.46					
VI	160	197	167	190	173	193	278	332	237	249					
Base stock Vk 100°C mm²/s	7.5	5.0	5.0	5.0	5.0	6.0	4.0	2.7	5.0	5.0					
(HTHS (capillary, 100°C) – HTHS (TBS, 100°C) / HTHS (TBS, 100°C))	0.03	0.06	0.06	0.06	0.06	0.06	0.17	0.19	0.10	0.10					
B mass%	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.033	0.020					
Ca mass%	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220	0.220					
P mass%	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096	0.096					
Zn mass%	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110	0.110					
N mass%	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.100					

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C L A I M S

1. Lubricating oil composition for diesel engines characterised in that it contains:

- 5 a) a GTL base oil with a kinematic viscosity at 100°C of 4.5 to 5.5 mm²/s,
b) a comb-like PMA (polymethacrylate) based viscosity index improver and
c) a boron-containing dispersant and/or boron-containing detergent, wherein the total amount of boron-containing dispersant and/or boron-containing detergent
10 incorporated in terms of conversion to boron content relative to the total amount of the composition being not less than 0.025 mass%,
and wherein it satisfies 0W-30 or 5W-30 in the SAE J300
15 standard.

2. Lubricating oil composition for diesel engines in accordance with Claim 1 which includes a non-comb-like PMA (polymethacrylate) based viscosity index improver and an SCP (styrene-diene copolymer) based viscosity index
20 improver and/or an OCP (olefin copolymer) based viscosity index improver, and which further satisfies at least one of the following (1) to (3).

(1) Non-comb-like PMA based viscosity index improver content/total viscosity index improver content: not more
25 than 0.7

(2) OCP based viscosity index improver content/total viscosity index improver content: not more than 0.2

(3) SCP based viscosity index improver content/total viscosity index improver content: not more than 0.3

30 [Claim 3]

3. Lubricating oil composition for diesel engines in

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accordance with Claim 1 or 2 satisfying the following viscosity characteristic:

$$\frac{[HTHS\ 100^{\circ}C\ viscosity\ (capillary\ method) - HTHS\ 100^{\circ}C\ viscosity\ (TBS\ method)]}{HTHS\ 100^{\circ}C\ viscosity\ (TBS\ method)} = 0.07\ to\ 0.15$$

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082719

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M169/04
ADD.

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)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/097152 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 2 July 2015 (2015-07-02) page 5, line 30 - page 6, line 4 page 8, line 27 - page 14, line 24 page 15, line 25 - page 24, line 20 page 29, line 20 - page 33, line 25 claims; examples	1-3
Y	EP 2 256 180 A1 (IDEMITSU KOSAN CO [JP]) 1 December 2010 (2010-12-01) paragraph [0008] - paragraph [0016] paragraph [0021] - paragraph [0025] claims; examples	1-3
	----- -/-	



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082719

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014/106998 A1 (NELSON KENNETH D [US] ET AL) 17 April 2014 (2014-04-17) paragraph [0011] - paragraph [0014] paragraph [0031] - paragraph [0040] claims; examples -----	1-3
Y	EP 2 164 885 A1 (EVONIK ROHMAX ADDITIVES GMBH [DE]) 24 March 2010 (2010-03-24) paragraph [0001] - paragraph [0003] paragraph [0016] - paragraph [0031] paragraph [0093] - paragraph [0109] paragraph [0117] - paragraph [0120] claims; examples -----	1-3
A	EP 2 000 523 A1 (CHEVRON ORONITE SA [FR]; CHEVRON ORONITE CO [US]) 10 December 2008 (2008-12-10) paragraph [0026] paragraph [0032] - paragraph [0074] paragraph [0082] - paragraph [0094] paragraph [0100] - paragraph [0101] claims; examples -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/082719

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015097152 A1	02-07-2015	CN 105849240 A EP 3087168 A1 JP 2017500426 A US 2017009180 A1 WO 2015097152 A1	10-08-2016 02-11-2016 05-01-2017 12-01-2017 02-07-2015
EP 2256180 A1	01-12-2010	BR PI0908558 A2 CN 101970626 A EP 2256180 A1 JP 5330716 B2 JP 2009221382 A TW 201002814 A US 2011077183 A1 WO 2009116438 A1	22-09-2015 09-02-2011 01-12-2010 30-10-2013 01-10-2009 16-01-2010 31-03-2011 24-09-2009
US 2014106998 A1	17-04-2014	CA 2746938 A1 CN 102300967 A EP 2376610 A2 JP 2012512308 A JP 2015071789 A JP 2016210998 A SG 172250 A1 US 2010152072 A1 US 2012145116 A1 US 2014106998 A1 WO 2010077755 A2	08-07-2010 28-12-2011 19-10-2011 31-05-2012 16-04-2015 15-12-2016 28-07-2011 17-06-2010 14-06-2012 17-04-2014 08-07-2010
EP 2164885 A1	24-03-2010	BR PI0813492 A2 CA 2693461 A1 CN 101687963 A EP 2164885 A1 ES 2462616 T3 JP 5502730 B2 JP 2010532805 A KR 20100032417 A RU 2010104028 A US 2010190671 A1 WO 2009007147 A1	06-01-2015 15-01-2009 31-03-2010 24-03-2010 26-05-2014 28-05-2014 14-10-2010 25-03-2010 20-08-2011 29-07-2010 15-01-2009
EP 2000523 A1	10-12-2008	CA 2632392 A1 CN 101372643 A EP 2000523 A1 JP 5344540 B2 JP 2008297547 A SG 148107 A1 US 2008300154 A1 US 2012142564 A1	30-11-2008 25-02-2009 10-12-2008 20-11-2013 11-12-2008 31-12-2008 04-12-2008 07-06-2012