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

(11) EP 2 574 657 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
03.04.2013 Bulletin 2013/14

(51) Int Cl.:
C10M 163/00 *(2006.01)* *C10N 30/06* *(2006.01)*
C10N 40/25 *(2006.01)*

(21) Application number: **12186481.3**

(22) Date of filing: **28.09.2012**

(84) Designated Contracting States:
AL 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 RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **29.09.2011 JP 2011214116**

(71) Applicant: **Chevron Japan Ltd.**
Chiyoda-ku
Tokyo 101-0041 (JP)

(72) Inventors:
- **Takeuchi, Yoshitaka**
  Omaezaki-shi, Shizuoka (JP)
- **Kawamura, Toshimi**
  Omaezaki-shi, Shizuoka (JP)
- **Sugimura, Takashi**
  Omaezaki-shi, Shizuoka (JP)

(74) Representative: **Nash, David Allan**
Haseltine Lake LLP
Redcliff Quay
120 Redcliff Street
Bristol
BS1 6HU (GB)

(54) **Lubricating oil composition**

(57) A lubricating oil composition which has a sulfur content of 0.5 wt.% or less and which at least comprises a base oil and the following additive components a) to e): a) an ashless dispersant comprising an alkenyl- or alkyl-succinimide or a derivative thereof; b) an ashless dispersant comprising an alkenyl- or alkyl-succinic ester or a derivative thereof; c) a molybdenum complex of a basic nitrogen-containing compound; d) an alkaline earth metal-containing detergent having TBN of 10-400 mg●≛ KOH/g; and e) an anti-wear agent favorably employed for lubricating internal combustion engines operated using a low sulfur hydrocarbon fuel.

EP 2 574 657 A1

Description

[0001] This application claims priority to Japanese Patent Application number JP 2011-214116 which was filed on September 29, 2011.

Field of Invention

[0002] The present invention relates to a lubricating oil composition favorably employable for lubricating internal combustion engines such as diesel engines and gasoline engines. In particular, the invention relates to a lubricating oil composition having a low sulfur content of about 0.5 wt.% or less, particularly about 0.2 wt.% or less, which reduces friction occurring in the internal combustion engines mounted to land-travelling automotives using low sulfur hydrocarbon fuel and shows good high temperature detergency.

Background of Invention

[0003] The sulfur contained in fuels such as gasolines or diesel fuels employed for operating internal combustion engines is oxidized when it bums in the engine to give sulfur oxide such as sulfuric acid. A portion of the sulfur oxide enter the lubricating oil employed for lubricating the engine, and the remaining portion is exhausted with other exhaust gases. The sulfur oxide exhausted with other exhaust gases causes environmental pollution. Hence, the sulfur content in the fuel has been heretofore under severe regulation. The regulation on the sulfur content was initially applied to gasolines (fuels for gasoline engines). However, the regulation on the sulfur content has been also applied recently to diesel fuels having a higher sulfur content. The sulfur content in the diesel fuels has been recently regulated to be not higher than 0.0010 wt.%.

[0004] As a result of the decrease of the sulfur content, the lubricating oil is less contaminated with sulfur oxide such as sulfuric acid which is produced when the fuel bums. This means that the amount of the overbasic metal-containing detergent in the lubricating oil can be reduced. The basic metal-containing detergent serves for neutralizing the sulfur oxide in the lubricating oil.

[0005] When the fuel bums in the engine, not only the fuel, but also a portion of the lubricating oil bums in the engine. A gas produced by burnt lubricating oil is also exhausted with other exhaust gas. Therefore, it is desirable to reduce the amount of the sulfur content of the lubricating oil.

[0006] By the way, the recently employed lubricating oils for internal combustion engines comprise a base oil (hydrocarbon oil having lubricating viscosity) and a variety of additives (i.e., lubricating oil additives) such as a basic metal-containing detergent for neutralizing the emigrated sulfur oxide, an oxidation inhibitor for keeping the base oil functioning at elevated temperature from deteriorating, a dispersant for dispersing soots produced by burning of fuels and residues produced by deterioration of the base oil and metal-containing detergent in the base oil, an extreme pressure agent for preventing of seizure of the piston and cylinder, a friction-reducing agent (friction modifier) for reducing friction occurring between the piston and cylinder.

[0007] Therefore, the phosphorus component and metal component contained in the additive placed in the lubricating oil composition are decomposed when the lubricating oil composition bums and enter the exhaust gas in the form of phosphorus oxides and metal oxides. The phosphorus oxides and metal oxides contained in the exhaust gas, are brought into contact with oxidative catalyst or reductive catalyst placed in the exhaust gas-cleaning apparatus and inactivate the catalyst.

[0008] For the reasons described above, it has been demanded to reduce the sulfated ash content, phosphorus content and sulfur content of the lubricating oil composition.

[0009] Patent publication 1 (JP 2002-53888 A) discloses a lubricating oil composition favorably employable for lubricating internal combustion engines operated using a fuel having a low sulfur content, particularly, diesel engines. The disclosed lubricating oil composition comprises a base oil having a sulfur content of 0.1 wt.% or less (preferably 0.03 wt.% or less) and the following additives:

a) an ashless dispersant comprising an alkenyl- or alkyl-succinimide or a derivative thereof in an amount of 0.01-0.3 wt.% in terms of the nitrogen content;
b) a metal-containing detergent having a sulfur content of 3 wt.% or less and a TBN of 10-350 mg•KOH/g in an amount of 0.1-1 wt.% in terms of the sulfated ash content;
c) a zinc dialkyldithio phosphate in an amount of 0.01-0.12 wt.% in terms of the phosphorus content;
d) an oxidation-inhibiting phenolic compound and/or an oxidation-inhibiting amine compound in an amount of 0.01-5 wt.%,

the lubricating oil composition having a sulfated ash content of 0.1-1 wt.%, a phosphorus content of 0.01-0.1, a sulfur

content of 0.01-0.3 wt.%, a chlorine content of 40 wt.ppm or less, and an organic acid salt derived from the metal-containing detergent in an amount of 0.2 to 7 wt.% (preferably 0.5-5 wt.%, more preferably 1.0-3 wt.%),
wherein the above-mentioned contents and amounts are expressed based on the total amount of the lubricating oil composition.

[0010] Patent Publication 1 further discloses in the working examples that the disclosed lubricating oil compositions show good high temperature detergency in the internal combustion engines.

[0011] Patent Publication 1 furthermore discloses that the lubricating oil composition may contain a molybdenum-containing compound which can serve as a friction modifier, an oxidation inhibitor as well as an anti-wear agent. The molybdenum-containing compound can be one of known molybdenum-containing compounds such as sulfoxymolybdenum dithiocarbamate, sulfoxymolybdenum dithiophosphate and molybdenum complexes of succinimide possibly containing sulfur.

[0012] Patent Publication 2 (JP 2004-149802 A) discloses a lubricating oil composition having a low sulfated ash content, a low phosphorus content and a low sulfur content, preferably employable for lubricating internal combustion engines (that is, engine oil), which comprises a base oil, an ethylene carbonate post-treated ashless dispersant, a borated ashless dispersant, an overbased metal-containing detergent and a phosphorus compound. Patent Publication 2 further discloses that the disclosed lubricating oil composition may contain a molybdenum-succinimide complex. In the working examples of Patent Publication 2, it is shown by experimental data that the lubricating oil composition shows good oxidation stability as well as good anti-wear performance.

[0013] Patent Publication 3 discloses a low sulfated ash, low phosphorus, low sulfur engine oil (engine oil composition) comprising a low sulfur base oil, a boron-containing ashless dispersant, a molybdenum-containing friction modifier, a metal-containing detergent such as sulfonate, phenate or salicylate, and a zinc dithiophosphate. The molybdenum-containing friction modifier can be molybdenum diorgano-dithiocarbamate, molybdenum diorgano-dithiophosphate, molybdenum carboxylate, and a trinuclear molybdenum compound such as $Mo_3S_7(dtc)_4$ or $Mo_3S_4(dtc)_4$. In the working examples, it is shown by the experimental data that the lubricating oil composition employing the above-mentioned trinuclear molybdenum compound has particularly good high temperature oxidation stability and a good friction reductive performance.

[0014] As is described above, it has been known that the molybdenum-containing compound is particularly effective as a friction modifier to be incorporated into lubricating oil compositions.

[0015] As the known molybdenum-containing compounds, molybdenum diorgano dithiocarbamate and molybdenum diorgano dithiophosphate are most generally employed. However, both compounds have disadvantage problems, in that the former contains sulfur (S) in its molecular structure and the latter contains phosphorous (P) in its molecular structure, and hence both produce poisonous gases such as sulfur oxide gas and phosphorus oxide gas when the lubricating oil burns in the internal combustion engine, resulting in inactivation of the catalysts of the exhaust gas-clearing apparatus. As is explained above, Patent Publication 3 describes that a trinuclear molybdenum compound such as $Mo_3S_7(dtc)_4$ or $Mo_3S_4(dtc)_4$ shows a good friction-modifying function (friction-reducing function). However, these trinuclear molybdenum compounds contains sulfur atoms in the molecular structure of its ligand moiety, i.e., dithiocarbamate, dtc, and further contains other sulfur atoms directly attached to the molybdenum atom, and hence, the trinuclear molybdenum compounds contains a relatively large amount of sulfur in the compound *per se.* Therefore, the trinuclear molybdenum compound is not favorably employed for incorporation into the lubricating oil composition if reduction of the sulfur content in the oil composition is intended.

Summary of Invention

[0016] Accordingly, it is the object of the invention to provide a molybdenum-containing friction-reducing agent having no or a relatively less amount of sulfur and phosphorus which is favorably employable in place of the conventionally employed friction-reducing agents containing sulfur and phosphorus in relatively large amounts, such as molybdenum diorgano-dithiocarbamate, molybdenum diorgano-dithiophosphate, molybdenum carboxylate, and a trinuclear molybdenum compound such as $Mo_3S_7(dtc)_4$ or $Mo_3S_4(dtc)_4$.

[0017] The present inventors have found that the friction-reducing function of the known molybdenum complex of a basic nitrogen-containing compound such as a molybdenum-succinimide complex is prominently enhanced if the molybdenum complex is incorporated into lubricating oil compositions in combination with specifically selected amounts of an alkenyl- or alkyl-succinimide or its derivative (which is known as an ashless dispersant) and an alkenyl- or alkyl-succinic acid ester (succinate) or its derivative (which is also known as an ashless dispersant).

[0018] The present invention has been made on the above-mentioned inventors' new finding. It has been further found out that the lubricating oil compositions containing the above-mentioned molybdenum complex of a basic nitrogen-containing compound but not containing the succinimide or its derivative (and further not containing the succinate or its derivative) show improved resistance to oxidation at high temperatures but the oil compositions show little reduction of the friction coefficient.

[0019] Accordingly, the present invention provides a lubricating oil composition for lubricating internal combustion engines which has a sulfur content of 0.5 wt.% or less and which comprises a base oil having a lubricating viscosity and at least the following additive components a) to e):

a) an ashless dispersant in an amount of 0.5-5.0 wt.% which comprises an alkenyl- or alkyl-succinimide or a derivative thereof;
b) an ashless dispersant in an amount of 0.5-5.0 wt.% which comprises an alkenyl- or alkyl-succinic ester or a derivative thereof;
c) a molybdenum complex of a basic nitrogen-containing compound in an amount of 50-1,200 wt.ppm in terms of a molybdenum content thereof;
d) an alkaline earth metal-containing detergent having a TBN in the range of 10 to 400 mg•KOH/g in an amount of 0.05-1.0 wt.% in terms of an alkaline earth metal content thereof; and
e) an anti-wear agent in an amount of 0.05-5.0 wt.%.

[0020] The present invention further provides a method for operating internal engines mounted to land-travelling vehicles using a fuel having a sulfur content of 0.001 wt.% or less under lubrication with the above-mentioned lubricating oil composition according to the invention.

[0021] Preferred embodiments of the invention are stated below.

(1) The lubricating oil composition has the sulfur content in the range of 0.01 to 0.2 wt.%.
(2) The lubricating oil composition has the sulfur content in the range of 0.05 to 0.12 wt.%.
(3) The lubricating oil composition is a multi-grade engine oil further comprising a viscosity index improver, whereby being classified to 0W5, 0W10, 0W15, 0W20, 0W30, 5W20, 5W30, 10W20, or 10W30.
(4) The lubricating oil composition contains the component a), namely, an alkenyl- or alkyl-succinimide or a derivative thereof, in an amount of 1.0-4.0 wt.%.
(5) The lubricating oil composition contains the component b), namely, an alkenyl- or alkyl-succinic ester or a derivative thereof, is contained in an amount of 1.0-4.0 wt.%.
(6) The lubricating oil composition wherein a ratio of the component a) to the component b) is in the range of 1:4 to 4:1.
(7) The component c), namely, a molybdenum complex of a basic nitrogen-containing compound, contains a sulfur not larger than 1 wt.%.
(8) The component c), namely, the molybdenum complex of a basic nitrogen-containing compound, contains a sulfur in the range of 0.05 to 0.5 wt.%.
(9) The component c) is a molybdenum complex of a succinimide.
(10) The component d) comprises an alkaline earth metal salicylate.
(11) The anti-wear agent is a zinc dialkyldithiophosphate.
(12) The lubricating oil composition further comprises an oxidation inhibitor.
(13) The lubricating oil composition is used for lubricating internal combustion engines operated using a fuel oil having a sulfur content of 0.001 wt.% or less.

[0022] The lubricating oil composition of the invention contains a molybdenum complex of a basic nitrogen-containing compound (serving as a friction-modifier) in combination of a mixture of known dispersants, that is, an alkenyl- or alkyl-succinimide or a derivative thereof and an alkenyl- or alkyl-succinic acid ester (succinate) or a derivative thereof both in specific amounts. Therefore, the lubricating oil composition can be prepared to contain sulfur at a low level. Nevertheless, the lubricating oil composition of the invention shows a prominently good friction-reducing function.

Detailed Description of Invention

[0023] The base oil and additives employable for the preparation of the lubricating oil composition of the invention are described below in more detail.

Base Oil

[0024] The base oil generally is a mineral oil or a synthetic oil showing a kinematic viscosity of 2 to 50 mm^2/s at 100°C. There are no specific limitations on the natures and other properties of the mineral oil and synthetic oil. However, the sulfur content of the base oil should be 0.1 wt.% or less. The sulfur content preferably is 0.03 wt.% or less, and more preferably is 0.005 wt.% or less.

[0025] The mineral oil preferably is an oil which is obtained by processing a lubricating oil distillate of a mineral oil by solvent refining, hydrogenation, or their combination. Particularly preferred is a highly hydrogenated refined oil (corresponding to a hydrocracked oil, typically has a viscosity index of 100 to 150, an aromatic component content of 5 wt.% or less, a nitrogen content of 50 wt.ppm or less, and a sulfur content of 50 wt. ppm or less. Particularly preferred is a high viscosity index base oil for instance having a viscosity index of 140-160 which is obtained by hydroisomerization of slack wax or GTL wax (Gas-To-Liquid).

[0026] Examples of the synthetic oils (synthetic lubricating base oils) include poly-α-olefin such as a polymerized compound of α-olefin having 3 to 12 carbon atoms; a dialkyl ester of a di-basic acid such as sebacic acid, azelaic acid or adipic acid and an alcohol having 4 to 18 carbon atoms, typically dioctyl sebacate; a polyol ester which is an ester of 1,1,1-trimethylolpropane or pentaerythritol and a mono-basic acid having 3 to 18 carbon atoms; and alkylbenzene having an alkyl group of 9 to 40 carbon atoms. The synthetic oil generally contains essentially no sulfur, shows good stability to oxidation and good heat resistance, and gives less residual carbon and soot when it is burned. Therefore, the synthetic oil is preferably employed for the lubricating oil composition of the invention. Particularly preferred is poly-α-olefin, from the viewpoint of the object of the invention.

[0027] Each of the mineral oil and synthetic oil can be employed singly. If desired, however, two or more mineral oils can be employed in combination, and two or more synthetic oils can be employed in combination. The mineral oil and synthetic oil can be employed in combination at an optional ratio.

Ashless Dispersant

[0028] The lubricating oil composition of the invention comprises at least two different ashless dispersants, that is, an alkenyl- or alkyl-succinimide or a derivative thereof (component a) and an alkenyl- or alkyl-succinic ester or a derivative thereof (component b), in an amount of 0.5-5.0 wt.%, preferably 1.0-4.0 wt.%, for each (the amount is based on the total amount of the lubricating oil composition). The component a) and component b) are preferably contained in a weight ratio of 1:4 to 4:1, more preferably 1:2 to 2:1.

[0029] The component a), namely, the alkenyl- or alkyl-succinimide or a derivative thereof, may be a known alkenyl- or alkyl-succinimide or a derivative thereof. For example, the alkenyl- or alkyl-succinimide derived from a polyolefin or its derivative may be employed. A representative succinimide can be prepared by the reaction between succinic anhydride substituted with a high molecular weight alkenyl or alkyl and a polyalkylene polyamine containing average 4 to 10 (preferably 5 to 7) nitrogen atoms in one molecule. The high molecular weight alkenyl or alkyl is preferably derived from a polybutene (particularly a high reactivity polybutene having a vinylidene terminal) having a number average molecular weight of about 900 to 3,000.

[0030] The process for obtaining the polybutenyl-succinic anhydride by the reaction of polybutene and maleic anhydride is generally performed by the chlorination process using a chloride compound. The chlorination process is advantageous in its reaction yield. However, the reaction product obtained by the chlorination process contains a large amount (for instance, approx. 2,000-3,000 wt.ppm) of chlorine. In contrast, if the thermal reaction process using no chloride compound is employed, the reaction product contains only an extremely small chlorine (for instance, 0-30 ppm). Accordingly, it is preferred that the succinimide be prepared from a polybutenyl succinic anhydride which is produced by the thermal reaction, whereby the chlorine content of the resulting succinimide is in the range of 0 to 30 wt.ppm. The succinimide can be reacted with boric acid, alcohol, aldehyde, ketone, alkylphenol, cyclic carbonate, organic acid or the like, to give a modified succinimide. Particularly, a borated alkenyl(or alkyl)-succinimide which is obtained by the reaction with boric acid or a boron compound is advantageous from the viewpoints of thermal and oxidation stability.

[0031] The component b), namely, the alkenyl- or alkyl-succinic ester or a derivative thereof, may be a known alkenyl- or alkyl-succinic ester or a derivative thereof. For example, the alkenyl- or alkyl-succinic ester derived from a polyolefin or its derivative may be employed. A representative succinic ester can be prepared by the reaction between succinic anhydride substituted with a high molecular weight alkenyl or alkyl and an alcohol containing average 1 to 6 hydroxyl groups in one molecule. The high molecular weight alkenyl or alkyl is preferably derived from a polybutene (particularly a high reactivity polybutene having a vinylidene terminal) having a number average molecular weight of about 900 to 3,000.

[0032] The lubricating oil composition of the invention may contain other ashless dispersants such as an alkenylbenzylamine ashless dispersant in addition to the ashless dispersant a) (i.e., component a)) and ashless dispersant b) (i.e., component b)).

Molybdenum complex of basic nitrogen-containing compound

[0033] The lubricating oil composition of the invention further comprises a molybdenum complex of a basic nitrogen-containing compound in an amount of 50-1,200 wt.ppm in terms of a molybdenum content thereof. This molybdenum complex is already known as a multifunctional addi-tive. The molybdenum complex of a basic nitrogen-containing compound may contain a small amount of sulfur.

[0034] The molybdenum complex of basic nitrogen-containing compound functions mainly as an oxidation inhibitor, an anti-wear agent or a friction modifier in the lubricating oil composition.

[0035] A preferred molybdenum complex of a basic nitrogen-containing compound is an oxymolybdenum complex produced by reaction of an acidic molybdenum compound and a basic nitrogen-containing compound. Examples of the acidic molybdenum compounds include molybdic acid, ammonium molybdate, and alkali metal salts of molybdate. Examples of the basic nitrogen-containing compounds include succinimide, carboxylic amide, hydrocarbylamine and a Mannich basic compound. Examples of the molybdenum complex of basic nitrogen-containing compounds include a molybdenum complex of succinimide and a molybdenum complex of a secondary aliphatic amine.

[0036] The molybdenum complex of a basic nitrogen-containing compound can be employed after reaction with a small amount of sulfur or a sulfur-containing compound. Specifically, a reaction product obtained by sulfurization of a molybdenum complex of succinimide at low temperatures. The reaction product preferably contains sulfur in a relatively small amount such as 10 wt.% or less. The sulfoxymolybdenum complex can be prepared in the manner described in Examples C to H of United States Patent 6,562,765 B.

[0037] The lubricating oil composition of the invention can further contain other molybdenum-containing compounds such as sulfoxymolybdenum dithiocarbamate, sulfoxymolybdenum dithiophosphate, and oxymolybdenum monoglyceride.

Alkaline earth metal-containing Detergent

[0038] The lubricating oil composition of the invention further comprises an alkaline earth metal-containing detergent having a TBN in the range of 10 to 400 mg•KOH/g in an amount of 0.05-1.0 wt.% in terms of an alkaline earth metal content thereof. The known alkaline earth metal-containing detergent having a TBN in the range of 10 to 400 mg•KOH/g is employable. Preferred is a calcium alkylsalicylate detergent. The calcium alkylsalicylate detergent preferably contains an organic acid salt in an amount of 0.2-7 wt.%, more preferably 0.5-5 wt.%, most preferably 1.0-3 wt.%. The calcium alkylsalicylate detergent preferably comprises an unsulfurized calcium alkylsalicylate detergent having an alkyl group containing 14-18 carbon atoms. The unsulfurized calcium alkylsalicylate detergent having an alkyl group containing 14-18 carbon atoms can be employed in combination with an unsulfurized calcium alkylsalicylate detergent having an alkyl group containing 20-28 carbon atoms. In the specification, the unsulfurized calcium alkylsalicylate detergent having an alkyl group containing 14-18 carbon atoms means an unsulfurized calcium alkylsalicylate detergent having an alkyl group in which 90 mole % or more of the alkyl groups contain 14-18 carbon atoms. The unsulfurized calcium alkylsalicylate detergent having an alkyl group containing 20-28 carbon atoms has the same meaning, that is, the unsulfurized calcium alkylsalicylate detergent having an alkyl group containing 20-28 carbon atoms means an unsulfurized calcium alkylsalicylate detergent having an alkyl group in which 90 mole % or more of the alkyl groups contain 20-28 carbon atoms.

[0039] The unsulfurized calcium alkylsalicylate preferably is a calcium salt of an alkylsalicylic acid which can be prepared from an alkylphenol (which is produced by the reaction of α-olefin having the desired number of carbon atoms and phenol) by the Kolbe-Schmidt reaction. Generally, the calcium salt of an alkylsalicylic acid can be overbased by the use of lime and carbon dioxide, to give an overbased calcium salicylate.

[0040] The calcium salt of an alkylsalicylate can be prepared by the steps of neutralizing phenol to give its calcium salt and subsequent carbonation.

[0041] The calcium alkylsalicylate detergent is preferably incorporated into the lubricating oil composition under such conditions that the amount of the organic acid salt (contained in the calcium alkylsalicylate detergent) is in the range of 0.2 to 7 wt.%, preferably 0.5 to 5 wt.%, more preferably 1.0 to 3 wt.%, based on the total amount of the lubricating oil composition. In more detail, the calcium alkylsalicylate detergent is an oily dispersion which comprises an organic acid metal salt (generally called a soap component) and basic inorganic salt micro-particles (e.g., calcium carbonate particles) aggregated around the organic acid metal salt in an oily medium. Generally, the dispersion contains the oily medium in an amount of 30 to 50 wt.%. Even if the amount of the calcium alkylsalicylate detergent is reduced, the high temperature detergency (i.e., power for keeping the inside space of an engine operated at high temperatures) of the lubricating oil composition does not substantially lower provided that the amount of the organic acid metal salt is kept at or above a certain level.

[0042] The alkaline earth metal-containing detergent can be an alkaline earth metal salt of an organic acid having a carbon-nitrogen bonding or a phenol derivative. This detergent can have a high TBN regardless of a sulfated ash content, if it is treated with an amine compound. The amine compound brings a base number originating from the basic nitrogen atoms. For example, a metal salt of an aminocarboxylic acid can be employed. Particularly preferred is an unsulfurized alkylphenate (i.e., alkaline earth metal salt) having a Mannich base structure. This compound can be obtained by Mannich reaction using an alkylphenol, formaldehyde, and an amine or an amine compound to give an aminomethylated phenol, and subsequent neutralization of the reaction product by a base such as calcium hydroxide.

[0043] Alternatively, the alkaline earth metal-containing detergent can be an alkaline earth metal salt of a sulfonic acid (i.e., sulfonate) obtained from a petroleum sulfonic acid, an alkylbenzenesulfonic acid, or an alkyltoluenesulfonic acid.

[0044] Alternatively, the alkaline earth metal-containing detergent can be a sulfurized phenate, namely, an alkaline earth metal salt of a sulfurized alkyl phenol

Anti-wear agent

[0045] The lubricating oil composition of the invention further comprises an anti-wear agent (component e)) in an amount of 0.05-5.0 wt.%. There are no specific limitation on the anti-wear agent, and the known sulfur-containing anti-wear agent as well as the known phosphorus-containing anti-wear agent can be employed. Examples of the sulfur-containing anti-wear agents include sulfurized olefin, polysulfide compound, sulfurized ester, sulfurized alcohol, sulfurized amide, sulfurized oil/fat, ashless dithiocarbamate, metal (other than molybdenum) dithiocarbamate, mercapto thiadiazole, mercapto benzothiadiazole, and mercapto thiazoline. Examples of the phosphorus-containing anti-wear agents include phosphoric acid ester, phosphorous acid ester, thiophosphoric acid ester, their amine salts, and their metal salts such as zinc dialkyldithiophosphate, zinc dialkyldithiophosphate, and zinc dialkylphosphate.

[0046] The anti-wear agent, i.e., component e), preferably is zinc dialkyldithiophosphate or zinc dihydrocarbylphosphate. These zinc phosphate anti-wear agents are well known and easily produced by the known procedures. The zinc phosphate anti-wear agent can be employed in an amount of 0.01-0.12 wt.%, but preferably in an amount of 0.01-0.06 wt.%, in consideration of the desired low phosphorus content and sulfur content.

[0047] The zinc dialkyldithiophosphate preferably contains an alkyl group having 3-18 carbon atoms or an alkylaryl group having C_{3-18} alkyl group. Most preferred is a zinc dialkyldithiophosphate containing an alkyl group derived from a secondary alcohol having 3-18 carbon atoms or a zinc dialkyldithiophosphate containing a mixture of alkyl groups derived from a mixture of a primary alcohol having 3-18 carbon atoms and a secondary alcohol having 3-18 carbon atoms. Both are particularly effective for reducing wear. A zinc dialkyldithiophosphate derived from a primary alcohol shows high thermal resistance. These zinc dialkyldithiophosphates can be employed alone or in combination in the form of a mixture mainly comprising one derived from the secondary alcohol and/or one derived from the primary alcohol.

Oxidation Inhibitor

[0048] The lubricating oil composition of the invention preferably contains an oxidation inhibitor in an amount of 0.01-5 wt.%, preferably 0.1-3 wt.%. The oxidation inhibitor can be the phenolic oxidation inhibitor and the amine oxidation inhibitor. A lubricating oil composition having a low sulfated ash content, a low phosphorus content and a low sulfur content is apt to show a relatively low high-temperature detergency, oxidation-inhibiting performance and anti-wear performance due to decrease of the amounts of the metal-containing detergent and zinc dithiophosphate. Therefore, the lubricating oil composition of the invention preferably contains an oxidation inhibitor so as to keep these performances high.

[0049] Preferred oxidation inhibitors are a diarylamine oxidation inhibitor and a hindered phenol oxidation inhibitor. These oxidation inhibitors also function for improving high-temperature detergency. The diarylamine oxidation inhibitor is advantageous in giving a base number originating from the nitrogen atoms. The hindered phenol oxidation inhibitor is advantageous in producing no NO_x gas.

[0050] Examples of the hindered phenol oxidation inhibitors include 2,6-di-t-butyl-p-cresol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-methylenebis(6-t-butyl-o-cresol), 4,4'-isopropylidenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-thiobis(2-methyl-6-t-butylphenol), 2,2-thio-diethylenebis [3-(3,5-di-t-butyl-4-hydoxyphenyl)propionate], octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, and octyl 3-(3,5-t-butyl-4-hydroxy-3-methylphenyl)propionate.

[0051] Examples of the diarylamine oxidation inhibitors include alkyldiphenylamine having a mixture of alkyl groups of 4 to 9 carbon atoms, p,p'-dioctyldiphenylamine, phenyl-α-naphthylamine, phenyl-α-naphthylamine, alkylated β-naphthylamine, and alkylated phenyl-α-naphthylamine.

[0052] Each of the hindered phenol oxidation inhibitor and diarylamine oxidation inhibitor can be employed alone or in combination. If desired, other oil soluble oxidation inhibitors can be employed in combination with the above-mentioned oxidation inhibitor(s).

Other Additives

[0053] The lubricating oil composition of the invention may further contain an alkali metal borate hydrate for increasing stability at high temperatures and a base number. A representative alkali metal borate hydrate can be prepared in the manner described in United States Patents 3,929,650 and 4,089,790. For example, the alkali metal borate hydrate can be in the form of a dispersion containing micro-particles of an alkali metal borate hydrate which is produced by carbonizing a neutral alkali metal or alkaline earth metal sulfonate in the presence of an alkali metal hydroxide to yield an overbased sulfonate and reacting the overbased sulfonate with boric acid. In the carbonizing procedure, it is desired to incorporate an ashless dispersant such as succinimide into the reaction mixture. The alkali metal preferably is potassium or sodium. The alkali metal borate hydrate can be a dispersion of $KB_3O_5 \cdot H_2O$ particles having a particle size of about 0.3 μm or less which is dispersed in the presence of a neutral calcium sulfonate and succinimide. From the viewpoint of resistance to hydrolysis, potassium is preferably replaced with sodium.

[0054] The lubricating oil composition of the invention preferably contains a viscosity index improver in an amount of 20 wt.% or less, preferably 1 to 20 wt.%. Examples of the viscosity index improvers are polymers such as polyalkyl methacrylate, ethylene-propylene copolymer, styrene-butadiene copolymer, and polyisoprene. A dispersant viscosity index improver and a multi-functional viscosity index improver which are produced by providing dispersing properties to the above-mentioned polymer are preferably employed. The viscosity index improvers can be used alone or in combination.

[0055] The lubricating oil composition of the invention may further contain a small amount of various auxiliary additives. Examples of the auxiliary additives are described below. benzotriazol compounds and thiadiazol compounds functioning as metal deactivating agent; nonionic polyoxyalkylene surface active agents such as polyoxyethylenealkylphenyl ether and copolymers of ethylene oxide and propylene oxide functioning as an anti-rust agent and an anti-emulsifying agent. In addition, various compounds functioning as an anti-foaming agent and a pour point depressant can be incorporated.

[0056] The above-mentioned auxiliary additives may be incorporated into the lubricating oil composition in an amount of 3 wt.% or less, particularly in an amount of 0.001-3 wt.%.

Examples

(1) Preparation of lubricating oil composition (test oil)

[0057] Lubricating oil compositions having a low sulfur content (0.5 wt.% or less) for evaluation on the oil performance were prepared in the below-described manner using the below-mentioned base oil and additives. The lubricating oil compositions were formulated to show a viscosity grade (SAE viscosity grade) of 5W30 by addition of a viscosity index improver.

(2) Base oil and additives

1) Base oil (mixture of the below-mentioned base stock A and base stock B in the weight ratio of 46:54)

[0058]

Base stock A: Hydrocracked base stock showing a kinematic viscosity of 6.4 mm^2/s (at 100°C), a viscosity index of 132, a saturated component content of 92 wt.% and a sulfur content of less than 0.001 wt.%.

Base stock B: Hydrocracked base stock showing a kinematic viscosity of 4.1 mm^2/s (at 100°C), a viscosity index of 127, a saturated component content of 92 wt.% and a sulfur content of less than 0.001 wt.%.

2) Additives

[0059] Ashless dispersant A: Ethylene carbonate post-treated succinimide dispersant (nitrogen content: 0.85 wt.%) prepared by the steps of thermally reacting polybutene (number average molecular weight: about 2,200) and maleic anhydride to give polyisobutenylsuccinic anhydride, reacting about 2 moles of the polyisobutenylsuccinic anhydride and polyalkylene polyamine containing 6.5 nitrogen atoms (average) in one molecule to give a bis-type succinimide, and finally treating the bis-type succinimide with ethylene carbonate under reaction.

[0060] Ashless dispersant B: Alkenylsuccinic ester (TAN: 5 mg•KOH/g) prepared by the steps of thermally reacting polybutene (number average molecular weight: about 1,000) and maleic anhydride to give polyisobutenylsuccinic anhydride, reacting about 1.14 moles of the polyisobutenylsuccinic anhydride and one mole of pentaerythritol.

[0061] Mo complex of succinimide: A product (Mo content: 4.5 wt.%, N content: 2.1 wt.%, S content: 0.16 wt.%) obtained by the steps of reacting a mono-type alkenylsuccinimide derived from polyisobutene having a number average molecular weight of about 1,000 and molybdic acid to give a molybdenum complex and reacting the molybdenum complex with a small amount of sulfur.

MoDTC: Sulfoxymolybdenum dialkyldithiocarbamate (Mo content: 10 wt.%, S content: 11 wt.%)

Ca-containing detergent A: Calcium monoalkylsalicylate (alkyl containing about 14-18 carbon atoms, overbase degree: 2.0, Ca content: 6.2 wt.%, S content: 0.12 wt.%)

Ca-containing detergent B: Calcium monoalkylsalicylate (alkyl containing about 20-28 carbon atoms, overbase degree: 8.2, Ca content: 11.4 wt.%, S content: 0.17 wt.%)

Ca-containing detergent C: Calcium sulfonate (neutral type, Ca content: 2.4 wt.%, sulfur content: 2.7 wt.%)

ZnDTP: zinc dialkyldithiophosphate (P content: 7.2 wt.%, S content: 14.4 wt.%, derived from a mixture of a secondary alcohol having 4 carbon atoms and a secondary alcohol having 6 carbon atoms)

Oxidation inhibitor: Mixture of dialkyldiphenylamine oxidation inhibitor and hindered phenol propionate oxidation inhibitor.
Viscosity index improver (VII): Non-dispersant type ethylene-propylene copolymer (Paratone 8057)

(3) Determination of friction coefficient

[0062] The friction coefficient was determined by means of High Frequency Reciprocating Rig (HFRR) under the below-described conditions:
[0063] Oil temperature: 105°C, Load: 400 g, Friction length: 1,000 μm, Reciprocating frequency: 20 Hz, Test Period: one hour.

(4) Evaluation of inhibition of production of high-temperature deposit

[0064] The power inhibiting production of a high-temperature deposit (Deposit) was evaluated by means a hot tube tester (HTT) under the below described conditions:
[0065] In a heater block was placed vertically a glass tube (inner diameter: 2 mm). The test oil and air were supplied into the tube from its bottom at supply rates of 0.31 cc/h and 10 cc/min., respectively. These procedures were performed under keeping the temperature of the heater element at 280°C for 16 hours. Thereafter, the glass tube was taken out from the heater block, washed with petroleum ether, and dried. The deposit attached to the inner surface of the glass tube was observed and marked according to the merit rating.
[0066] The merit rating was done in the known manner on the basis of 10 points. The higher point means that the power of inhibiting production of deposit is high.

(5) Compositions of the test oils and results of determination and evaluation

[0067] The test results of the test oils are set forth in Table 1 below.

Table 1

Base oil/ Additives	Example 1	Com. Ex. 1	Com. Ex. 2
Ashless dispersant A (wt.%)	3.0	5.5	3.0
Ashless dispersant B (wt.%)	2.5	-	2.5
Succinimide Mocomplex (Mo wt. ppm)	220	220	-
MoDTC (Mo wt.ppm)	-	-	220
Ca detergent A (Ca wt.%)	0.19	0.19	0.19
Ca detergent B (Ca wt.%)	0.06	0.06	0.06
Ca detergent C (Ca wt.%)	0.01	0.01	0.01
ZnDTP (P wt.%)	0.04	0.04	0.04
Oxidation inhibitor (wt.%)	1.0	1.0	1.0
VII (wt.%)	5.0	5.0	5.0
Base oil	remainder	remainder	remainder
S content (wt.%)	0.11	0.11	0.13
Friction coefficient	0.05	0.12	0.05
HTT merit point	7.5	7.5	5.5

Remarks:

[0068] The test results set forth in Table 1 indicate the following:
[0069] The lubricating oil composition of the invention comprising succinimide-Mo complex, succinimide dispersant (Ashless dispersant A) and succinic ester dispersant (Ashless dispersant B) in combination (Test oil of Example 1) shows the same high-temperature deposit production-inhibiting power but markedly low friction coefficient as compared with the lubricating oil composition (Test oil of Comparison Example 1) comprising the succinimide-Mo complex and succinimide dispersant (Ashless dispersant A) in combination but containing no succinic ester dispersant (Ashless dispersant B). Test oil of Comparison Example 2 prepared by replacing the succinimide-Mo complex with the same amount of MoDTC (sulfoxy molybdenum dialkyldithiocarbamate) shows the same friction coefficient but poor power of inhibiting

production of high-temperature deposit.

Claims

1. A lubricating oil composition for lubricating internal combustion engines which has a sulfur content of 0.5 wt.% or less and which comprises a base oil having a lubricating viscosity and at least the following additive components a) to e):

   a) an ashless dispersant in an amount of 0.5-5.0 wt.% which comprises an alkenyl- or alkyl-succinimide or a derivative thereof;
   b) an ashless dispersant in an amount of 0.5-5.0 wt.% which comprises an alkenyl- or alkyl-succinic ester or a derivative thereof;
   c) a molybdenum complex of a basic nitrogen-containing compound in an amount of 50-1,200 wt.ppm in terms of a molybdenum content thereof;
   d) an alkaline earth metal-containing detergent having a TBN in the range of 10 to 400 mg•KOH/g in an amount of 0.05-1.0 wt.% in terms of an alkaline earth metal content thereof; and
   e) an anti-wear agent in an amount of 0.05-5.0 wt.%.

2. The lubricating oil composition of claim 1, wherein the sulfur content is in the range of 0.01 to 0.2 wt.%.

3. The lubricating oil composition of claim 1, wherein the sulfur content is in the range of 0.05 to 0.12 wt.%.

4. The lubricating oil composition of claim 1, which is a multi-grade engine oil further comprising a viscosity index improver, whereby being classified to OW5, OW10, OW15, OW20, OW30, SW20, SW30, 10W20, or 10W30.

5. The lubricating oil composition of claim 1, wherein the component a) is contained in an amount of 1.0-4.0 wt.%.

6. The lubricating oil composition of claim 1, wherein the component b) is contained in an amount of 1.0-4.0 wt.%.

7. The lubricating oil composition of claim 1, wherein the ratio of the component a) to the component b) is in the range of 1:4 to 4:1.

8. The lubricating oil composition of claim 1, wherein the component c) contains sulfur not larger than 1 wt.%.

9. The lubricating oil composition of claim 1, wherein the component c) contains sulfur in the range of 0.05 to 0.5 wt.%.

10. The lubricating oil composition of claim 1, wherein the component c) is a molybdenum complex of a succinimide.

11. The lubricating oil composition of claim 1, wherein the component d) comprises an alkaline earth metal salicylate.

12. The lubricating oil composition of claim 1, wherein the anti-wear agent is a zinc dialkyldithiophosphate.

13. The lubricating oil composition of claim 1, which further comprises an oxidation inhibitor.

14. The lubricating oil composition of claim 1, which is employed for lubricating internal combustion engines operated using a fuel oil having a sulfur content of 0.001 wt.% or less.

15. A method for operating internal engines mounted to land-travelling vehicles using a fuel having a sulfur content of 0.001 wt.% or less under lubrication with the lubricating oil composition of claim 1.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 12 18 6481

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 2008/234153 A1 (MATSUI SHIGEKI [JP]) 25 September 2008 (2008-09-25) * paragraphs [0001], [0291] - paragraph [0312]; claim 1; examples 1-5; table 1 * -----	1-15	INV. C10M163/00 ADD. C10N30/06 C10N40/25
Y	GB 1 506 786 A (SHELL INT RESEARCH) 12 April 1978 (1978-04-12) * page 3, line 30 - page 4, line 9; example V * -----	1-15	
A	US 2010/331224 A1 (BOFFA ALEXANDER B [US] ET AL) 30 December 2010 (2010-12-30) * examples 6-10; table 2 * -----	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	7 January 2013	Pöllmann, Klaus

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 18 6481

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-01-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008234153 A1	25-09-2008	NONE	
GB 1506786 A	12-04-1978	BE 851615 A1	18-08-1977
		FR 2341358 A1	16-09-1977
		GB 1506786 A	12-04-1978
		JP 1378198 C	08-05-1987
		JP 52102892 A	29-08-1977
		JP 61046174 B	13-10-1986
US 2010331224 A1	30-12-2010	CA 2645411 A1	20-06-2009
		EP 2078745 A1	15-07-2009
		JP 2009149890 A	09-07-2009
		SG 153756 A1	29-07-2009
		SG 173314 A1	29-08-2011
		US 2009163392 A1	25-06-2009
		US 2010331224 A1	30-12-2010
		US 2012184473 A1	19-07-2012

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2011214116 A **[0001]**
- JP 2002053888 A **[0009]**
- JP 2004149802 A **[0012]**
- US 6562765 B **[0036]**
- US 3929650 A **[0053]**
- US 4089790 A **[0053]**