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(54) Lubricating oil composition

(57) A lubricating oil composition having a low sulfated ash content, a low P content, a low S content and a low Cl content and being favorably employable for lubricating a diesel engine operated using a hydrocarbon fuel oil having a low S content, comprises the following components a) to d) dissolved or dispersed in a base oil having a low S content: a) an ashless dispersant such as alkenyl- or alkylsuccinimide or its derivative, b) a calcium alkylsalicylate detergent having a low S content and containing an organic acid calcium salt, which is a mixture of an unsulfurized calcium alkylsalicylate detergent having a C_{14}-C_{18} alkyl group and an unsulfurized calcium alkylsalicylate detergent having a C_{20}-C_{28} alkyl group, c) a zinc phosphate anti-wear agent, and d) an oxidation inhibitor.

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Description

[0001] This application claims priority to Japanese Patent Application number JP 2010-201229 which was filed on September 8, 2010.

Field of the Invention

[0002] The present invention relates to a lubricating oil composition favorably employable for lubricating an internal combustion engine operated overland such as a diesel engine, a gasoline engine or a gas engine. In more detail, the invention relates to a lubricating oil composition for internal combustion engines which has a low sulfated ash content, a low phosphorus content and a low sulfur content and shows good high temperature detergency and anti-wear performance, and which gives less adverse effects to an exhaust gas cleaning apparatus such as a particulate filter or an oxidation catalyst mounted on a car for oxidizing unburnt soot, fuel and lubricating oil contained in exhausted gas, so that the lubricating oil composition can comply with the recently adopted severe exhaust gas requirements and further can comply with more severe exhaust gas requirements which are probably adopted in future.

[0003] In particular, the invention provides an environment friendly lubricating oil composition for internal combustion engines which is favorably employable with vehicles operated using hydrocarbon fuel oil having a sulfur content of not more than approximately 0.005 wt.%, particularly not more than approximately 0.001 wt.%, specifically diesel engine-mounted vehicles equipped with exhaust gas-cleaning apparatuses such as a particulate filter and an oxidation catalyst.

Background of the Invention

[0004] Recently, it has become very important for overland running diesel engine mounted vehicles to reduce environmental pollution caused by exhaust gas components such as particulates and NO_x. It is known that the pollution can be reduced by mounting exhaust gas-cleaning apparatuses such as a particulate filter and an oxidation catalyst onto the vehicles. It is noted, however, that the particulate filter is plugged with metal oxides, sulfated ash and carboxylic acids produced by the combustion of the conventional lubricating oil compositions having a high sulfated ash content, a high phosphorus content and a high sulfur content, though the soot adsorbed on the filter are removed by oxidation and burning in the exhaust gas cleaning apparatus.

[0005] In addition, it is now required to reduce a sulfur content in a fuel oil because the sulfur in the fuel oil is burnt to produce unfavorable products such as sulfuric acid and sulfate in the exhaust gas which gives adverse effects to the oxidation catalyst. For instance, the sulfur content of diesel fuel oils for diesel engine-mounted vehicles has decreased from not more than approximately 0.005 wt.% to not more than approximately 0.001 wt.%. When the sulfur content in the fuel oil decreases, the content of the metal-containing detergent serving for neutralizing the sulfuric acid or the like in the lubricating oil composition can be decreased. It is known that a portion of the lubricating oil composition is burnt in the engine and incorporated into the exhaust gas. Therefore, it is preferred that the metal content and sulfur content in the lubricating oil composition be as low as possible. Moreover, it is preferred that the phosphorus content in the lubricating oil composition is decreased so as to keep the catalyst from deteriorating. Furthermore, it is preferred that the chlorine content in the lubricating oil composition is decreased so as to keep the exhaust gas from being contaminated with dioxine.

[0006] Heretofore, the diesel engines employed overland for motor cars, construction machines and electric generators have been operated generally using a fuel oil (light oil or heavy oil) having a sulfur content of approximately 0.005 wt. % or more and a lubricating oil composition having a sulfated ash content of approximately 1.3 to 2 wt.%, a sulfur content of approximately 0.3 to 0.7 wt.%, and a phosphorus content of approximately 0.1 to 0.13 wt.%.

[0007] JPA 2002-53888 (corresponding to US 2002/0019320 A1) discloses a lubricating oil composition which satisfies the recent requirements of low sulfated ash content, low phosphorus content, low sulfur content and low chlorine content, which is employable for diesel engines operated using a fuel oil having a low sulfur content. In more detail, JPA 2002-53888 discloses a lubricating oil composition having a sulfur content of 0.01 to 0.3 wt.% and a phosphorus content of 0.01 to 0.1 wt.%, and giving a sulfated ash in the range of 0.1 to 1 wt.%, which comprises

a) a major amount of a mineral base oil having a sulfur content of at most 0.1 wt.%, preferably at most 0.03 wt.%;
b) an ashless dispersant comprising an alkenyl- or alkyl-succinimide or a derivative thereof in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen atom content;
c) a metal-containing detergent containing an organic acid metal salt which is selected from the group consisting of a non-sulfurized alkali metal or alkaline earth metal salt of an alkylsalicylic acid having a TBN of 10 to 350 mg KOH/g and a non-sulfurized alkali metal or alkaline earth metal salt of an alkylphenol derivative having a Mannich base structure, in an amount of 0.1 to 1 wt.% in terms of a sulfated ash content;
d) a zinc dialkyldithiophosphate in an amount of 0.01 to 0.1 wt.% in terms of a phosphorus content; and

e) an oxidation inhibitor selected from the group consisting of a phenol compound and an amine compound in an amount of 0.01 to 5 wt.%,

wherein the amount is calculated based on the amount of the lubricating oil composition.

[0008] It is further described that a preferred metal-containing detergent is an alkali metal salt or an alkaline earth metal salt of unsulfurized alkylsalicylic acid having an alkyl group having a mean carbon atom number of approx. 8 to 30.

[0009] In the recently established JASO M 355:2008 (for lubricating oil for automotive diesel engines), it is described that the lubricating oil according to DH-2-08 for trucks and buses equipped with a post-treatment apparatus for complying with the exhaust gas regulation ought to have a sulfated ash content of 1.0±0.1 wt.%, a phosphorus content of not more than 0.12 wt.%, a sulfur content of not more than 0.5 wt.% and a chlorine content of not more than 150 ppm.

[0010] It is an object of the present invention to provide a lubricating oil composition for internal combustion engines, which satisfies the requirements of the abovementioned JASO M 355:2008 and shows improved high temperature detergency at 300°C or higher, as compared with the lubricating oil composition disclosed in the aforementioned JPA 2002-53888, so as to sufficiently comply with the anticipated more severe engine operation conditions such as operations at elevated temperatures.

Summary of the Invention

[0011] The present inventors have studied the lubricating oil composition described in JPA 2002-53888 for improving the high temperature detergency attained by the disclosed lubricating oil composition and found that the improved high temperature detergency at temperatures of 300°C or higher is accomplished by a lubricating oil composition in which a mixture of an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms is employed for the unsulfurized alkaline earth metal alkylsalicylate having an alkyl group having a mean carbon atom number of approx. 8 to 30. The so formulated lubricating oil composition shows a satisfactorily good anti-wear performance and a satisfactorily low viscosity at low temperatures so that the lubricating oil composition is favorably employable in cold districts. The present invention has been made on this finding by the present inventors.

[0012] Accordingly, the present invention resides in a lubricating oil composition for lubricating an internal combustion engine which is operated by the use of a fuel oil having a sulfur content of not more than 0.005 wt.%, particularly not more than 0.001 wt.%, comprising the following components a) to d) dissolved or dispersed in a base oil having a sulfur content of not more than 0.1 wt.%, preferably not more than 0.03 wt.%, and has a sulfated ash content in a range of 0.1 to 1.1 wt.%, a phosphorus content in a range of 0.01 to 0.12 wt.%, a sulfur content in a range of 0.01 to 0.5 wt.% and a chlorine content of not more than 150 ppm:

a) an ashless dispersant in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen content, the ashless dispersant being selected from the group consisting of an alkenyl succinimide, an alkyl succinimide, or derivatives thereof;
b) a calcium alkylsalicylate detergent in an amount of 0.1 to 1 wt.% in terms of a sulfated ash content, the calcium alkylsalicylate detergent having a sulfur content of not more than 3 wt.% and a total base number in the range of 10 to 350 mg KOH/g, containing an organic acid calcium salt under the condition that the lubricating oil composition contains the organic acid calcium salt in an amount of 0.2 to 7 wt.%, preferably 0.5 to 5 wt.%, more preferably 1.0 to 3 wt.%, based on the amount of the oil composition, and comprising a mixture of an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms;
c) a zinc phosphate anti-wear agent in an amount of 0.01 to 0.12 wt.% in terms of a phosphorus content, the zinc phosphate being selected from the group consisting of a zinc dialkyldithiophosphate and a zinc dihydrocarbylphosphate, and
d) an oxidation inhibitor in an amount of 0.01 to 5 wt.%, the oxidation inhibitor being selected from the group consisting of an oxidation inhibiting phenol compound and an oxidation inhibiting amine compound,

wherein the sulfated ash content, phosphorus content, sulfur content, and the wt.% given in a) to d) above are values based on the amount of the lubricating oil composition.

[0013] The lubricating oil composition of the invention has a low sulfated ash content, a low phosphorus content and a low sulfur content similar to those of the lubricating oil composition disclosed in the aforementioned JPA 2002-53888 but shows an improved high temperature detergency at temperatures of 300°C or higher. Further, the lubricating oil composition of the invention shows a high anti-wear performance. Furthermore, the lubricating oil composition of the invention shows a satisfactorily low viscosity at low temperatures, so that the lubricating oil composition can be favorably employed in cold districts.

[0014] Therefore, the lubricating oil composition of the invention is particularly favorably employable for lubricating

diesel engines which are mounted onto motor cars equipped with exhaust gas cleaning apparatus such as a particulate filter and an oxidation catalyst and which are operated in cold districts, using a hydrocarbon fuel oil having a sulfur content of not more than approx. 0.005 wt.%, specifically not more than approx. 0.001 wt.%.

Detailed Description of the Invention

[0015] The preferred embodiments of the invention are set forth below.

(1) The calcium alkylsalicylate detergent of the component b) has a total base number in the range of 30 to 300 mg KOH/g.
(2) The unsulfurized calcium alkylsalicylate detergent having an alkyl group having a carbon atom number of 14 to 18 has a total base number in the range of 100 to 250 mg KOH/g.
(3) The unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms has a total base number in the range of 280 to 350 mg KOH/g.
(4) The calcium alkylsalicylate detergent comprises a mixture of the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms in a ratio of 2:8 to 8:2, specifically 3:7 to 7:3, in terms of a calcium content ratio, namely, a ratio of the amounts of calcium contained in respective detergents.
(5) The calcium alkylsalicylate detergent comprises a mixture of the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms in a ratio of 4:6 to 8:2, specifically 5:5 to 7:3, in terms of a ratio of a content of the organic acid calcium salt, namely, a ratio of the amounts of the organic acid calcium salt contained in the respective detergents.
(6) The ashless dispersant of the component a) comprises succinimide or a derivative thereof which is obtained by a reaction of a polybutenylsuccinic anhydride with a polyamine, the polybutenylsuccinic anhydride being obtained by a thermal reaction of polybutene and maleic anhydride in the absence of chlorine or a chlorine-containing compound.
(7) The lubricating oil composition contains a molybdenum-containing compound in an amount of 0.01 to 5 wt.%.
(8) The lubricating oil composition has a total base number in the range of 1 to 17 mg KOH/g, specifically 2 to 13 mg KOH/g.
(9) The lubricating oil composition is a multigrade engine oil containing a viscosity index improver and is an oil of 0W5, 0W10, 0W15, 0W20, 0W30, 5W20, 5W30, 10W20, or 10W30.
(10) The lubricating oil composition is employed for lubricating a diesel engine operated using a fuel oil having a sulfur content of not more than 0.005 wt.%, specifically not more than 0.001 wt.%, in which the diesel engine is mounted on an overland-running vehicle.

[0016] The invention further resides in a method for operating a diesel engine by the use of a fuel oil having a sulfur content of not more than 0.005 wt.%, specifically not more than 0.001 wt.%. and a lubricating oil composition of the invention, the diesel engine being mounted on an overland-running vehicle.

Base Oil

[0017] The base oil employable for the lubricating oil composition generally is a mineral oil or a synthetic oil having a kinetic viscosity of 2 to 50 mm^2/s at 100°C and the sulfur content is not more than 0.1 wt.%, preferably not more than 0.03, more preferably not more than 0.005 wt.%.

[0018] The mineral oil can be produced by processing a lubricating oil grade distillate by solvent refining and/or hydrotreating or hydrocracking. Preferably employed is a super-hydrogenating base oil, such as, a base oil having a viscosity index in the range of 100 to 150, an aromatic content of 5 wt.% or lower, and nitrogen and sulfur contents of 50 ppm or lower. Particularly preferred is a high viscosity index base oil having a viscosity index of 140-160 which is obtainable by hydrogenation and isomerization of slack wax or GTL wax.

[0019] A synthetic oil (synthetic base oil) can be poly-α-olefin, namely a polymer of α-olefin having a carbon atom number of 3-12; dialkyl esters which are esters of a dibasic acid such as sebacic acid, azelaic acid or adipic acid with an alcohol having a carbon atom number of 4-18, for instance, dioctyl sebacate; polyol esters of 1-trimethylolpropane or pentaerithritol with a monobasic acid having a carbon atom number of 3-18; or an alkylbenzene having an alkyl group having a carbon atom number of 9-40. The synthetic oil is favorably employable, because the synthetic oil generally has almost no sulfur content and shows high oxidation stability and high thermal stability at high temperatures, and further produces less amounts of residual carbonaceous material and soots.

[0020] The mineral base oil and synthetic base oil can be employed singly. However, a combination of two or more

mineral base oils and a combination of two or more synthetic base oils can be employed. In addition, a mineral base oil and a synthetic base oil can be employed in combination in an optionally determined ratio.

Additional Lubricating Oil Additives

[0021] The ashless dispersant employed in the lubricating oil composition of the invention as the component b) can be an alkenylsuccinimide, an alkylsuccinimide, or a derivative thereof, in which the alkenyl group and alkyl group can be derived from polyolefin. The ashless dispersant is incorporated into the lubricating oil composition in an amount of 0.01 to 0.3 wt.% in terms of the nitrogen content. The percent is given per the amount of the lubricating oil composition. A representative succinimide can be obtained by the reaction between succinic anhydride having a substituent group of a high molecular weight alkenyl or alkyl with a polyalkylene polyamine having a mean nitrogen atom number of 4 to 10, preferably 5 to 7. The high molecular weight alkenyl or alkyl is preferably derived from polybutene having a number average molecular weight of approx. 900 to 3,000.

[0022] In the process for producing a polybutenyl succinic anhydride by the reaction of polybutene and maleic anhydride, a chlorination procedure is generally employed. However, the chlorination procedure gives a remaining chlorine in the product, and hence the finally produced succinimide inevitably contains a large amount (such as approx. 2,000 to 3,000 ppm) of the emigrated chlorine. In contrast, the thermal reaction using no chlorine gives a final product having an extremely small chlorine content (such as 0 to 30 ppm). Therefore, the succinimide derived from a polyisobutenyl succinimide obtained by the thermal reaction can be favorably employed for formulating a lubricating oil composition having a low chlorine content such as 0 to 30 wt. ppm. The succinimide can be post-treated with boric acid, a boron-containing compound, alcohol, aldehyde, ketone, alkylphenol, cyclic carbonate or an organic acid. Preferred is a borated alkenyl- (or alkyl-) succinimide which is obtained by the post-treatment with boric acid or a boron-containing compound and which shows high thermal stability and high oxidation stability.

[0023] In the lubricating oil composition, the alkenyl- or alkyl-succinimide or its derivative is necessarily contained. However, other ashless dispersants such as alkenylbenzyl compounds or alkenylsuccinic esters can be employed in combination with the alkenyl- or alkyl-succinimide or its derivative.

[0024] The calcium alkylsalicylate detergent of the component b) necessarily contained in the lubricating oil composition of the invention contains an organic acid calcium salt to give the lubricating oil composition containing the organic acid calcium salt in an amount of 0.2 to 7 wt.%, preferably 0.5 to 5 wt.%, more preferably 1.0 to 3 wt.%, and comprises a mixture of an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms. In the invention, the "unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms" is used to mean an unsulfurized calcium alkylsalicylate detergent having an alkyl group in which at least 90 molar % of the alkyl group has 14 to 18 carbon atoms. Similarly, the "unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms" is used to mean an unsulfurized calcium alkylsalicylate detergent having an alkyl group in which at least 90 molar % of the alkyl group has 20 to 28 carbon atoms.

[0025] The unsulfurized calcium alkylsalicylate detergent preferably is a calcium alkylsalicylate prepared from an alkyl phenol (which is prepared from α-olefin having the desired carbon atom number and phenol) by way of Kolbe-Schmitt reaction. Generally, an overbased calcium salicylate which is obtained by way of the carbonation process using slaked lime and carbon dioxide gas for overbasing is used as the calcium salicylate detergent.

[0026] Otherwise, the calcium alkylsalicylate can be directly produced by carbonizing an alkylphenol calcium salt obtained by direct neutralization.

[0027] The metal-containing detergent may contain a small amount of an organic acid having a carbon-nitrogen bonding or a an alkali metal salt or an alkaline earth metal salt of a phenol derivative. Generally, a metal-containing detergent can have an increased base number by attaching an amine compound by reaction so that the base number derived by the basic nitrogen atom of the amine compound can contribute increase of the base number of the detergent. Therefore, a metal-containing detergent having a low sulfated ash but a high base number can be obtained. For instance, there may be mentioned various compounds such as a metal salt of an aminocarboxylic acid. Particularly, there can be mentioned an unsulfurized alkylphenate (alkali metal salt or alkaline earth metal salt) having a Mannich base structure. This compound can be prepared from an alkylphenol, formaldehyde, and an amine or an aminated compound via Mannich reaction to as to aminomethylate the phenol ring and subsequently neutralizing the reaction product with a base such as calcium hydroxide.

[0028] In addition to the heretofore described metal-containing detergents, a small amount of sulfonates such as alkali metal salts or alkaline earth metal salts of petroleum sulfonic acid, alkylbenzenesulfonic acid or alkyltoluenesulfonic acid can be employed in combination with the alkylsalicylate detergent.

[0029] The sulfurized phenate which has been used for the conventional diesel engine oils is an alkali metal salt or an alkaline earth metal salt of a sulfurized alkylphenol. Typically, calcium salt and magnesium salt are employed. The sulfurized phenate shows high thermal stability but generally has a high sulfur content such as approx. 3 wt.% or more,

which is brought about by the sulfurization reaction. In the invention, a small amount of the sulfurized phenate may be employed in combination with the alkylsalicylate detergent.

[0030] In the lubricating oil composition of the present invention, the two calcium alkylsalicylate detergents can be incorporated in combination under the condition that the organic acid calcium salts contained in these detergents are incorporated to give a lubricating oil composition containing the organic acid calcium salt in an amount of 0.2 to 7 wt.%, preferably 0.5 to 5 wt.%, more preferably 1.0 to 3 wt.%, based on the amount of the lubricating oil composition. The amount of the organic acid calcium salt can be adjusted by adjusting the content of the organic acid calcium salt in the detergent and/or adjusting the amount of the detergent to be incorporated into the lubricating oil composition.

[0031] It is known that the calcium alkylsalicylate detergent is an oily dispersion comprising an organic acid calcium salt (generally referred to as "soap content") and aggregated basic inorganic salt particles (typically calcium carbonate particles) surrounding the organic calcium salt dispersed in the oily medium (generally contained in an amount of approx. 25 to 55 wt.%). The amount of the organic acid calcium salt in the lubricating oil composition is important for keeping the high temperature detergency (ability for keeping the inside of the engine operated at high temperatures clean) at a high level.

[0032] The zinc phosphate anti-wear agent of the component c) is selected from the group consisting of a zinc dialkyldithiophosphate and a zinc dihydrocarbylphosphate.

[0033] These zinc phosphate anti-wear agents are well known, so far as their preparation methods and properties. The zinc phosphate anti-wear agent is employed in an amount of 0.01 to 0.12 wt.% in terms of a phosphorus content. However, the amount preferably is in the range of 0.01 to 0.06, so as to decrease the phosphorus content and sulfur content in the lubricating oil composition.

[0034] The zinc dialkyldithiophosphate preferably has an alkyl group having a carbon atom number of 3 to 18 or an alkylaryl group having an alkyl group of a carbon atom number of 3 to 18. Particularly preferred is a zinc dialkyldithiophosphate having an alkyl group derived from a secondary alcohol having a carbon atom number of 3 to 18 or having an alkyl group mixture derived from a mixture of a primary alcohol having a carbon atom number of 3 to 18 and a secondary alcohol having a carbon atom number of 3 to 18, both of which bring about very good anti-wear performance. The zinc dialkyldithiophosphate derived from the primary alcohol shows high thermal stability. These zinc dithiophosphates can be employed alone but can be employed in combination which mainly comprise one derived from the secondary alcohol and one derived from the primary alcohol.

[0035] The lubricating oil composition of the present invention further contains an oxidation-inhibiting phenol compound and/or an oxidation-inhibiting amine compound in an amount of 0.01 to 5 wt.%, preferably in an amount of 0.1 to 3 wt.%. Generally, a lubricating oil composition having a low sulfated ash content, a low phosphorus content and a low sulfur content contains decreased amounts of a metal-containing detergent and a zinc dithiophosphate, and hence shows decreases in high temperature detergency, oxidation stability and wear resistance. In order to improve these decreases, it is required to incorporate the component d) into the lubricating oil composition. The component d) preferably is a diarylamine oxidation inhibitor and/or a hindered phenol oxidation inhibitor. The incorporation of these oxidation inhibitor is effective to improve the high temperature detergency. From one aspect, the diarylamine oxidation inhibitor is preferred because it shows a base number derived from the contained nitrogen. From other aspect, the hindered phenol oxidation inhibitor is preferred because it efficiently inhibit oxidation caused by NO_x.

[0036] 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-hydroxyphenyl)propionate], octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate and octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate.

[0037] Examples of the diarylamine oxidation inhibitors include an alkyldiphenylamine having a mixed alkyl group having 4 to 9 carbon atoms, p,p'-dioctyldiphenylamine, phenyl-α-naphthylamine, phenyl-β-naphthylamine, alkylated α-naphthylamine, and alkylated phenyl-α-naphthylamine.

[0038] Each of the hindered phenol oxidation inhibitor and diarylamine oxidation inhibitor can be employed alone or in combination. Optionally, other oil-soluble oxidation inhibitors can be used in combination with the abovementioned oxidation inhibitors.

[0039] The lubricating oil composition of the present invention may further contain a multi-functional additive such as molybdenum-containing compound and/or a hydrated alkali metal borate in an amount of not more than 5 wt.%, particularly in an amount of 0.01 to 5 wt.%, per each. Most of these compounds have a sulfated ash content and a sulfur content. Therefore, the amount can be adjusted in consideration of the sulfated ash content and sulfur content of the resulting lubricating oil composition.

[0040] The molybdenum-containing compound serves mainly as a friction modifier, an oxidation inhibitor and an anti-wear agent in the lubricating oil composition, and further serves to improve the high temperature detergency. The molybdenum-containing compound is preferably incorporated into the lubricating oil composition in an amount of 10 to 2,500 ppm in terms of a molybdenum metal content. Examples of the molybdenum-containing compounds include a

sulfur-containing a succinimide-molybdenum complex compound, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum dithiophosphate, an amine-molybdenum complex compound, oxymolybdenum diethylatetamide, and oxymolybdenum monoglyceride. Particularly, the succinimide-molybdenum complex compound is effective to give improved high temperature detergency.

[0041] The hydrated alkali metal borate is effective in giving improved high temperature detergency and increased base number to the lubricating oil composition. The hydrated alkali metal borate can be prepared by the processes disclosed U.S. Patent Nos. 3,929,650 and 4,089,790. Preferred is a dispersion in which micro particles of an alkali metal borate are dispersed which can be prepared by carbonizing neutral alkali metal or alkaline earth metal sulfonate in the presence of an alkali metal hydroxide to give an overbased sulfonate and reacting the overbased sulfonate with boric acid. In the carbonation reaction, an ashless dispersant such as succinimide is preferably present in the reaction mixture. The alkali metal preferably is potassium or sodium. In more detail, particles of a product having a constitutional formula of $KB_3O_5 \cdot H_2O$ and a mean diameter of approx. 0.3 μm or less which are dispersed in a mixture of neutral calcium sulfonate and succinimide detergent can be mentioned. In consideration of resistance to water, potassium can be replaced with sodium.

[0042] The lubricating oil composition of the present invention preferably contains a viscosity index improver in an amount of 20 wt.% or less, more preferably in an amount of 1 to 20 wt.%. Examples of the viscosity index improvers include polymers such as polyalkyl methacrylate, ethylene-propylene copolymer, styrenebutadiene copolymer and polyisoprene. A dispersant type viscosity index improver or a multi-functional viscosity index improver obtained by attaching a dispersable group to the viscosity index improving polymer. The viscosity index improver can be employed singly or in combination.

[0043] The lubricating oil composition of the present invention can further contain a variety of auxiliary additives. Examples of the auxiliary additives include zinc dithiocarbamate, methylenebis(dibutyldithiocarbamate), an oil-soluble copper compound, a sulfur compound (such as sulfurized olefin, sulfurized ester or polysulfide), phosphate ester, phosphite ester, and organic amide compounds (e.g., oleylamide), which can serve as oxidation inhibitors or anti-wear agents. Further, benzotriazole compounds and thiadiazole compounds which serve as metal-inactivaters can be incorporated. Furthermore, a polyoxyalkylene type nonionic surfactant such as polyoxyethylene alkylphenyl ether or a copolymer of ethylene oxide and propylene oxide, which serves as a rust inhibitor or an anti-emulsifier. Furthermore, various amines, amides, amine salts or their derivatives, or fatty acid esters of a polyvalent alcohol or their derivatives, which can serve as friction modifiers can be incorporated. A variety of compounds which can serve as defoaming agents or pour point depressants can be incorporated. These auxiliary additives are preferably incorporated into the lubricating oil composition in an amount of not more than 3 wt.%, preferably in an amount of 0.001 to 3 wt.%.

Examples

[0044] The present invention is further described by the following illustrative non-limiting working examples.

(1) Preparation of lubricating oil compositions

[0045] The lubricating oil compositions for evaluating their performances were prepared from the below-mentioned base oil and additives, to give lubricating oil composition having a sulfated ash content of 1.0 wt.%, a phosphorus content of 0.09 wt.%, a sulfur content of 0.2 wt.% and a chlorine content of less than 5 ppm. To the lubricating oil composition was added a viscosity index improver to have a viscosity grade (SAE viscosity grade) of 5W30.

(2) Base oil and Additives

1) Base oil (a mixture of the following Base oil A and Base oil B in a volume ratio of 35:65)

[0046] Base oil A: Super-hydrogenated base oil (kinematic viscosity at 100°C: 4.0 mm^2/s, viscosity index: 123, sulfur content: less than 0.001 wt.%)

[0047] Base oil B: Super-hydrogenated base oil (kinematic viscosity at 100°C: 6.5 mm^2/s, viscosity index: 132, sulfur content: less than 0.001 wt.%)

2) Additives

[0048] Dispersant A: Ethylene carbonate post-treated succinimide dispersant (nitrogen content: 0.85 wt.%, chlorine content: 30 wt.ppm) prepared according to the procedure described in Example 17 of JP 7-150166 A, by the steps of reacting polybutene having a number average molecular weight of approx. 2,200 with maleic anhydride under the thermal reaction conditions; reacting the reaction product with polyalkylenepolyamine having an average nitrogen atom number

of 6.5 (per molecule) to give bis-type succinimide, and treating the succinimide with ethylene carbonate: 0.0085 wt.% (amount in terms of nitrogen content)

[0049] Dispersant B: Boron-containing succinimide dispersant (nitrogen content: 1.5 wt.%, boron content: 0.5 wt.%, chlorine content: less than 5 wt.ppm) prepared according to the procedure described in Example 8 of JP 7-150166 A, by the steps of reacting polybutene having a number average molecular weight of approx. 1,300 with maleic anhydride under the thermal reaction conditions; reacting the reaction product with polyalkylenepolyamine having an average nitrogen atom number of 6.5 (per molecule) to give bis-type succinimide, and treating the succinimide with boric acid: 0.06 wt.% (amount in terms of nitrogen content)

[0050] Calcium alkylsalicylate detergent (described hereinafter in Examples 1 & 2 and Comparison Example 1): 0.82 wt.% (amount in terms of sulfated ash content)

[0051] ZnDTP: Zinc dialkyldithiophosphate (P: 7.2 wt.%, Zn: 7.85 wt.%, S: 14.4 wt.%, derived from secondary alcohol having 3 to 8 carbon atoms): 0.09 wt.% (amount in terms of P content)

[0052] Oxidation inhibitor A: Amine compound (dialkyldi-phenylamine (alkyl: mixture of C_4 alkyl and C_8 alkyl), N: 4.6 wt.%, TBN: 180 mg KOH/g): 0.7 wt.%

[0053] Oxidation inhibitor B: Phenolic compound (octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate): 0.7 wt.%

[0054] Mo-containing compound: Sulfurized oxymolybdenum-succinimide complex compound (Mo: 5.4 wt.%, S: 3.7 wt.%, TBN: 45 mg KOH/g): 0.85 wt.%

[0055] Viscosity index improver: Non-dispersant type ethylene-propylene copolymer, Paratone 8057)

Example 1

[0056] A lubricating oil composition (TBN: 9.6 mg KOH/g, organic acid calcium salt content: 1.1 wt.%) was prepared using a 1:1 mixture (in terms of calcium content ratio) of the following two calcium alkylsalicylate detergents:

Unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms (TBN 220 mg KOH/g, petroleum medium content: approximately 30 wt.%, organic acid calcium salt content: 49 wt.%)
Unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms (TBN 320 mg KOH/g, petroleum medium content: approx. 35 wt.%, organic acid calcium salt content: 32.5 wt.%)

Example 2

[0057] A lubricating oil composition (TBN: 9.6 mg KOH/g, organic acid calcium salt content: 1.1 wt.%) was prepared using a 1:1 mixture (in terms of calcium content ratio) of the following two calcium alkylsalicylate detergents:

Unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms (TBN 225 mg KOH/g, petroleum medium content: at most approximately 30 wt.%, organic acid calcium salt content: 51 wt.%)
Unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms (TBN 320 mg KOH/g, petroleum medium content: approximately 35 wt.%, organic acid calcium salt content: 32.5 wt.%)

Comparative Example 1

[0058] A lubricating oil composition (TBN: 9.6 mg KOH/g, organic acid calcium salt content: 0.7 wt.%) was prepared using the following calcium alkylsalicylate detergent:

Unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms (TBN 320 mg KOH/g, petroleum medium content: approximately 35 wt.%, organic acid calcium salt content: 32.5 wt.%)

[0059] The determination of the organic acid calcium salt content (soap content) and evaluations of high temperature detergency and anti-wear performance were made by the following methods.

(1) Determination of organic acid calcium salt content (soap content)

[0060] The detergent was subjected to the conventional dialysis using rubber membrane to separate mineral oil and low molecular weight components out. The remaining residue (A) was an effective detergent component. Separately, the carbon dioxide content of the detergent was determined. Based on the carbon dioxide content and a separately determined calcium content, the content of calcium carbonate (overbasing component content (B)) was determined. The organic acid calcium salt (soap component) was calculated by subtracting (B) from (A).

(2) Evaluation of high temperature detergency

[0061] The lubricating oil composition was subjected to the below-mentioned hot tube test (KES-07-803) at 300°C and 305°C.

[0062] A glass tube (inner diameter: 2 mm) was placed in a heater block vertically. In the glass tube, the lubricating oil composition and air were supplied from the bottom of the tube at rates of 0.31 cc/hr. and 10 cc/min., respectively. The supply was continued for 16 hours maintaining the heater block at the predetermined temperature. After the supply was terminated, the glass tube was taken out and examined for deposition produced on the inner surface of the tube. The evaluation was performed on the basis of 10 points (maximum). The 10 point means that no deposition was observed.

(3) Evaluation of anti-wear performance

[0063] The anti-wear performance was examined by way of the Shell four ball test (described in JPI-5S-32) under the load of 40 kgf, at an oil temperature of 90°C, at 1,800 rpm and for the period of 30 minutes. The results are shown in terms of the diameter (mm) of wear area.

(4) Low temperature viscosity

[0064] The low temperature viscosity (cP) was determined by means of the MRV viscometer (described in ASTM D4684) at -35°C.

Results of Evaluations and Determination

[0065]

Oil	High temp. 300°C detergency	305°C	Anti-wear performance	Low temp. viscosity
Example 1	6.0	5.0	0.610	25,200
Example 2	6.0	5.0	-	25,100
Comparative Example 1	5.0	3.0	0.610	unmeasurable

[0066] As is seen from the above-mentioned results, the lubricating oil compositions according to the invention (Examples 1 and 2) containing the two calcium alkylsali-cylates having alkyl groups having different carbon atom numbers gave improved high temperature detergency under very severe temperature conditions such as 300°C and 305°C, and showed good anti-wear performance, and further showed a low viscosity at the low temperature. In contrast, the lubricating oil composition of Comparative Example 1 containing only one calcium alkylsalicylate having an alkyl group having 20 to 28 carbon atoms gave inferior high temperature detergency and could not show a satisfactorily low viscosity at the low temperature (that is, too viscous to measure), though the anti-wear performance was good

Claims

1. A lubricating oil composition for lubricating an internal combustion engine which is operated by the use of a fuel oil having a sulfur content of not more than 0.005 wt.%, which comprises the following components a) to d) dissolved or dispersed in a base oil having a sulfur content of not more than 0.1 wt.% and has a sulfated ash content in a range of 0.1 to 1.1 wt.%, a phosphorus content in a range of 0.01 to 0.12 wt.%, a sulfur content in a range of 0.01 to 0.5 wt.% and a chlorine content of not more than 150 ppm:

   a) an ashless dispersant in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen content, the ashless dispersant being selected from the group consisting of an alkenyl succinimide, an alkyl succinimide, or derivatives thereof;
   b) a calcium alkylsalicylate detergent in an amount of 0.1 to 1 wt.% in terms of a sulfated ash content, the calcium alkylsalicylate detergent having a sulfur content of not more than 3 wt.% and a total base number in the range of 10 to 350 mg KOH/g, containing an organic acid calcium salt under the condition that the lubricating oil composition contains the organic acid calcium salt in an amount of 0.2 to 7 wt.% based on the amount of the oil composition, and comprising a mixture of an unsulfurized calcium alkylsalicylate detergent having an

alkyl group having 14 to 18 carbon atoms and an unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms;
c) a zinc phosphate anti-wear agent in an amount of 0.01 to 0.12 wt.% in terms of a phosphorus content, the zinc phosphate being selected from the group consisting of a zinc dialkyldithiophosphate and a zinc dihydrocarbylphosphate, and
d) an oxidation inhibitor in an amount of 0.01 to 5 wt.%, the oxidation inhibitor being selected from the group consisting of an oxidation inhibiting phenol compound and an oxidation inhibiting amine compound,

wherein the sulfated ash content, phosphorus content, sulfur content, and the wt.% given in a) to d) above are values based on the amount of the lubricating oil composition.

2. The lubricating oil composition of claim 1, wherein the calcium alkylsalicylate detergent of the component b) has a total base number in the range of 30 to 300 mg KOH/g.

3. The lubricating oil composition of claim 1, wherein the unsulfurized calcium alkylsalicylate detergent having an alkyl group having a carbon atom number of 14 to 18 has a total base number in the range of 100 to 250 mg KOH/g.

4. The lubricating oil composition of claim 1, wherein the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms has a total base number in the range of 280 to 350 mg KOH/g.

5. The lubricating oil composition of claim 1, wherein the calcium alkylsalicylate detergent comprises a mixture of the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms in a ratio of 2:8 to 8:2, in terms of a calcium content ratio.

6. The lubricating oil composition of claim 1, wherein the calcium alkylsalicylate detergent comprises a mixture of the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 14 to 18 carbon atoms and the unsulfurized calcium alkylsalicylate detergent having an alkyl group having 20 to 28 carbon atoms in a ratio of 4:6 to 8:2, in terms of a ratio of a content of the organic acid calcium salt.

7. The lubricating oil composition of claim 1, wherein the ashless dispersant of the component a) comprises succinimide or a derivative thereof which is obtained by a reaction of a polybutenylsuccinic anhydride with a polyamine, the polybutenylsuccinic anhydride being obtained by a thermal reaction of polybutene and maleic anhydride in the absence of chlorine or a chlorine-containing compound.

8. The lubricating oil composition of claim 1, which contains a molybdenum-containing compound in an amount of 0.01 to 5 wt.%.

9. The lubricating oil composition of claim 1, wherein the lubricating oil composition has a total base number in the range of 1 to 17 mg KOH/g.

10. The lubricating oil composition of claim 1, which is a multi-grade engine oil contains a viscosity index improver and is an oil of 0W5, OW10, 0W15, 0W20, 0W30, 5W20, 5W30, 10W20, or 10W30.

11. The lubricating oil composition of claim 1, which is employed for lubricating a diesel engine operated using a fuel oil having a sulfur content of not more than 0.005 wt.%, the diesel engine being mounted on an overland-running vehicle.

12. A method for operating a diesel engine by the use of a fuel oil having a sulfur content of not more than 0.005 wt.% and a lubricating oil composition of claim 1, the diesel engine being mounted on an overland-running vehicle.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 18 0360

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 2002/019320 A1 (NAKAZATO MORIKUNI [JP] ET AL) 14 February 2002 (2002-02-14) * paragraphs [0009], [0018], [0036]; claim 1 *	1-12	INV. C10M163/00 ADD. C10N30/08 C10N30/04 C10N40/25
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TECHNICAL FIELDS SEARCHED (IPC)
C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 December 2011	Bertrand, Samuel

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