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(54) **Titre : COMPOSITION D'HUILE LUBRIFIANTE A ECONOMIE DE CARBURANT POUR MOTEUR DIESEL**
(54) **Title: FUEL ECONOMY LUBRICATING OIL COMPOSITION FOR LUBRICATING DIESEL ENGINES**

(57) **Abrégé/Abstract:**
A lubricating oil composition for internal combustion engines comprising a base oil having and lubricating viscosity and additives composed of a) a salt of an alkali metal or alkaline earth metal and an alkylsalicylate and/or an alkylcarboxylate, b) a nitrogen atom-containing ashless dispersant and/or a nitrogen atom-containing dispersive viscosity index improver, c) a neutral salt of a fatty acid and a fatty amine, and d) oxidation inhibitor, is effective for lubricating diesel engines using a low sulfur-content fuel, even though it has a low sulfated ash content, a low sulfur content and a low phosphorus content.

ABSTRACT OF DISCLOSURE

A lubricating oil composition for internal combustion engines comprising a base oil having and lubricating viscosity and additives composed of a) a salt of an alkali metal or alkaline earth metal and an alkylsalicylate and/or an alkylcarboxylate, b) a nitrogen atom-containing ashless dispersant and/or a nitrogen atom-containing dispersive viscosity index improver, c) a neutral salt of a fatty acid and a fatty amine, and d) oxidation inhibitor, is effective for lubricating diesel engines using a low sulfur-content fuel, even though it has a low sulfated ash content, a low sulfur content and a low phosphorus content.

Fuel Economy Lubricating Oil Composition For Lubricating Diesel Engines

Field of Invention

The present invention relates to a lubricating oil composition for lubricating internal combustion engines, particularly, a diesel engine. More specifically, the invention relates to a lubricating oil composition suitably employable for lubricating a diesel engine mounted to a car driven using fuel of a low sulfur content and enabling operation of the diesel engine with high fuel economy.

Background of the Invention

Heretofore, for gasoline engines it has been desired to develop and formulate lubricating oil compositions having a low sulfated ash content, a low sulfur content and a low phosphorus content to cope with the exhaust gas regulations applied to cars to which a gasoline engine is mounted. Similarly for diesel engines, in order to cope with the recent severe exhaust gas regulations, there arises a demand for developing and formulating a lubricating oil composition having a low sulfated ash content, a low sulfur content and a low phosphorus content for lubricating a diesel engine mounted to cars that are equipped with an exhaust gas cleaning apparatus and are driven by the use of a low sulfur fuel such as low sulfur content diesel fuel, bio-diesel fuel, or dimethyl ether.

Conventional lubricating oil compositions employed for lubricating a gasoline engine or a diesel engine generally comprise a major amount of a base oil having a lubricating viscosity and various additive components, depending upon specific function or formulators requirements. Examples of commonly formulated additive components include a metal-containing detergent, metal containing multifunctional addititves, ashless compounds such as ashless dispersant, oxidation inhibitors, etc.

The metal-containing detergent has a function to neutralize sulfuric acid produced by burning fuel and is necessarily incorporated into a lubricating oil composition for lubricating a diesel engine which uses a fuel having a higher sulfur content as compared with a fuel used for a gasoline engine. Generally, the metal-containing detergent is incorporated into a lubricating oil composition for diesel engines in an amount of TBN (total base number) in the range of 2 to 15 mg•KOH/g.

Zinc dithiophosphates (particularly, zinc dihydrocarbyldithiophosphate and zinc dialkyldithiophosphoate) which have multiple functions such as wear inhibition and extreme pressure resistance have been almost necessarily employed for preparation of the lubricating oil composition for diesel engines. In addition, zinc dihydrocarbylphosphate has been recently developed as a multi-functional additive replacing the zinc dithophosphate.

The above-mentioned multi-functional additives, however, have a drawback in having all of a metal element, a sulfur element, and a phosphorus element. Therefore, it is necessary to limit the amount of these multifunctional additives when the lubricating oil compositions having a low sulfated ash content, a low sulfur content, and a low phosphorus content are formulated.

On the other hand, the requirements concerning fuel economy have been increased for cars to which a gasoline engine or a diesel engine is mounted. The fuel economy can be mostly improved by modifying the structure of the engines. However, it is also known that the improvement of a lubricating oil composition is also effective to improve the fuel economy. Therefore, lubricating oil compositions employing a base oil of decreased oil viscosity or an improved friction modifier have been studied. Until now, a number of friction modifiers have been developed for internal combustion engines. Among the recently developed friction modifiers, sulfur-containing organic molybdenum compound friction modifiers such as molybdenum dithiocarbamate (MoDTC) and molybdenum dithiophosphate (MoDTP) show a practically satisfactory friction modifying function and hence are used widely. However, the sulfur-containing organic molybdenum compound friction modifiers also have drawbacks in having a metal element and a sulfur element. Moreover, the sulfur-containing organic molybdenum compound friction modifiers have additional drawbacks in that the friction reducing function disappears within a relatively short period of time, additionally these compounds are quickly rendered ineffective with soot loading.

Japanese Patent Provisional Publication 2004-155881 describes a fuel economy-type lubricating oil composition for internal combustion engines. The lubricating oil composition is prepared by combining a base oil having a viscosity index of 110 or more, a whole aromatic component content in the range of 2 to 15 wt.% and a sulfur content of 0.05 wt.% or more and a mixture of 1.2 to 5.0 wt.% of a fatty acid ester-type ashless friction modifier and/or a fatty amine-type ashless friction modifier and 0.02 to 0.15 wt.% (in terms of phosphorus content) of zinc dialkyldithiophosphate. It is described that the disclosed lubricating oil composition shows an improved friction reducing function, an improved wear resistance, and an improved storage stability. However, these types of frictions modifers have not been found to be effective at higher soot loading in the engines oil.

Summary of the invention

The lubricating oil composition of the invention has a low sulfated ash content, a low phosphorus content and a low sulfur content and show an excellent friction-modifying function (friction -reducing function) even in the case in that a large amount of soots have migrated in the lubricating oil composition Further, the lubricating oil composition of the invention causes no corrosion of the metallic engine parts. The corrosion of the metallic engine parts is a problem known in the lubricating oil compositions containing an amine compound and a fatty acid.

Accordingly, disclosed is a lubricating oil composition for lubricating internal combustion engines which has a sulfated ash content of 1.1 wt.% or less, a sulfur content of 0.5 wt.% or less, and a phosphorus content of 0.12 wt.% or less and which comprises a base oil having a lubricating viscosity and the following additive components:

a) a metal-containing detergent comprising at least one of an alkali metal or alkaline earth metal alkylsalicylate and an alkali metal or alkaline earth metal alkylcarboxylate in an amount of 0.01 to 0.4 wt.% in terms of an amount of metal contained in the composition;

b) at least one of a nitrogen-containing ashless dispersant and a nitrogen-containing dispersive viscosity index improver in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen amount;

c) a neutral salt of a fatty acid with a fatty amine in an amount of 0.1 to 5 wt.%; and

d) an oxidation inhibitor in an amount of 0.1 to 5 wt.%.

The lubricating oil composition of the invention is favorably employable for lubricating diesel engines mounted to cars which are driven using a low sulfur fuel. Moreover, the lubricating oil composition of the invention is very advantageous as a lubricating oil composition for lubricating diesel engines demonstrating high fuel economy. Particularly for diesel engines which are expected to experience a high soot loading in the lubricating oil, such as for diesel engines equipped with EGR system or a diesel engine using a lubricating oil with a long service period, the lubricating oil compositions of the present invention can extend the service life and maintain the fuel economy. In such an event a preferred friction modifier is a neutralized salt of a fatty acid having 8 to 30 carbon atoms and a fatty amine having 8 to 30 carbon atoms. In this regard the fatty acid is an unsaturated fatty acid, such as a linear chain fatty acid, more preferably oleic acid; while the fatty amine is a saturated linear chain fatty amine, more preferably stearyl amine. Typically the neutral salt of a fatty acid with a fatty amine is contain in an amount to provide a friction modifying effect, more preferably in an amount of 0.1 to 2 wt.%. Soot loading in the lubricating oil composition can be greater than 0.5 wt%, such as greater than 1 wt%, or greater than 2 wt%, up to about 5 wt%.

Thus, the lubricating oil composition of the invention is also advantageous as a lubricating oil composition for lubricating gasoline engines with high fuel economy.

In another aspect, there is provided a lubricating oil composition for lubricating internal combustion engines which has a sulfated ash content of 1.1 wt.% or less, a sulfur content of 0.5 wt.% or less, and a phosphorus content of 0.12 wt.% or less and which comprises a base oil having a lubricating viscosity and the following additive components:

a) a metal-containing detergent comprising at least one of an alkali metal or alkaline earth metal alkylsalicylate and an alkali metal or alkaline earth metal alkylcarboxylate in an amount of 0.01 to 0.4 wt.% in terms of an amount of metal contained in the composition;

b) at least one of a nitrogen-containing ashless dispersant and a nitrogen-containing dispersive viscosity index improver in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen amount;

c) a neutral salt of a fatty acid having 8 to 30 carbon atoms with a fatty amine having 8 to 30 carbon atoms in an amount of 0.1 to 5 wt.%; and

d) an oxidation inhibitor in an amount of 0.1 to 5 wt.%.

Detailed Description of the Invention

The present invention is directed in part to fuel economy lubricating oil compositions particularly suited for diesel engines. More specifically the components have been selected to impart a high friction modifying function (high friction reducing function) in the use for lubricating diesel engines, particularly diesel engines mounted to cars driven using a low sulfur content diesel fuel.

Although a lubricating oil composition for gasoline engines and a lubricating oil composition for diesel engines both are classified into a lubricating oil composition for internal combustion engines, there are some differences in the required lubricating functions. For instance, in the case of a lubricating oil composition for diesel engines, there is a problem in that produced soots likely migrate into the lubricating oil. The soots easily agglutinate to form hard solid mass, which disturbs lubrication in the engine. The resulting lowering of lubricating function causes decrease of fuel economy. In the case of a diesel engine equipped with EGR system or a diesel engine using a lubricating oil with a long service period, a large amount of soots are apt to migrate into the lubricating oil. Therefore, for the lubricating oil composition for diesel engines, the lubricating oil composition should show enough friction modifying function (friction reducing function) less influenced by the migration of soots. However, in consideration of the aforementioned requirements for the low sulfated ash content, low sulfur content and low phosphorus content, the conventionally employed zinc dithiophosphate should not be used in a large amount.

Known friction modifiers quickly lose their intended function when the lubricating oil becomes loaded with soot. Numerous friction modifier mechanisms and formulations using the friction modifiers in response to soot loading were investigated. Surprisingly, it has been discovered that a neutral salt of a fatty acid and a fatty amine is incorporated as a friction modifier into a lubricating oil composition containing a metal-containing detergent, an ashless dispersant and an oxidation inhibitor in which the metal-containing detergent is an alkali metal or alkaline earth metal salicylate or an alkali metal or alkaline earth metal alkylcarboxylate, the resulting lubricating oil composition show a satisfactory friction-reducing function even in the case that a large amount of soots have migrated in the lubricating oil composition. The herein-disclosed invention has been made on the basis of the above-mentioned discovery.

There is provided by the present invention a lubricating oil composition for lubricating internal combustion engines which has a sulfated ash content of 1.1 wt.% or less, a sulfur content of 0.5 wt.% or less, and a phosphorus content of 0.12 wt.% or less and which comprises a base oil having a lubricating viscosity and the following additive components:

a) a metal-containing detergent comprising at least one of an alkali metal or alkaline earth metal alkylsalicylate and an alkali metal or alkaline earth metal alkylcarboxylate in an amount of 0.01 to 0.4 wt.% in terms of an amount of metal contained in the composition;

b) at least one of a nitrogen-containing ashless dispersant and a nitrogen-containing dispersive viscosity index improver in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen amount;

c) a neutral salt of a fatty acid with a fatty amine in an amount of 0.1 to 5 wt.%; and

d) an oxidation inhibitor in an amount of 0.1 to 5 wt.%.

Particular aspects of lubricating oil compositions according to the invention are described below:

(1) The neutral salt of a fatty acid with a fatty amine is a neutralized salt of a fatty acid having 8 to 30 carbon atoms and a fatty amine having 8 to 30 carbon atoms.

(2) The fatty acid is an unsaturated fatty acid and the fatty amine is a saturated fatty amine.

(3) The fatty acid is an unsaturated linear chain fatty acid (particularly oleic acid).

(4) The fatty amine is a saturated linear chain fatty amine (particularly stearyl amine).

(5) The neutral salt of a fatty acid with a fatty amine is contained in an amount of 0.1 to 2 wt.%.

(6) The metal-containing detergent comprising at least one of an alkali metal or alkaline earth metal alkylsalicylate and an alkali metal or alkaline earth metal alkylcarboxylate is contained in an amount of 0.1 to 0.4 wt.% in terms of an amount of metal contained in the composition.

(7) The base oil having a lubricating viscosity has a saturated component of 85 wt.% or more, a viscosity index of 110 or more, and a sulfur content of 0.01 wt.% or less.

(8) The nitrogen-containing ashless dispersant has a weight average molecular weight in the range of 4,500 to 20,000.

(9) The lubricating oil composition further comprises a zinc dihydrocarbyldithiophosphate or a zinc dihydrocarbylphosphate in an amount of 0.01 to 0.12 wt.% in terms of an amount of a phosphorus amount.

(10) The lubricating oil composition has a TBN in the range of 2 to 15 mg•KOH/g and is used for lubricating diesel engines.

(11) The lubricating oil has a sulfur content in the range of 0.01 to 0.3 wt.%, particularly 0.01 to 0.2 wt.%.

(12) The nitrogen-containing ashless dispersant is bissuccinimide or polysuccinimide.

(13) The oxidation inhibitor is selected from the group consisting of phenolic oxidation inhibitors and amine oxidation inhibitors.

(14) The oxidation inhibitor is an oxymolybdenum complex compound with a basic nitrogen-containing compound (particularly succinimide).

(15) The metal-containing detergent further comprises an alkali metal or alkaline earth metal sulfonate and/or an alkali metal or alkaline earth metal phenate.

(16) The lubrication oil composition is of SAE viscosity grade of 0W20, 0W30, 0W40, 5W20, 5W30, 5W40, 10W20 or 10W30.

(17) A diesel engine is activated using the lubricating oil composition of the invention.

The base oil and additive components used for formulating the lubricating oil composition of the invention are described below in more detail.

Base oil

The base oil of the lubricating oil composition according to the invention is a mineral oil and/or a synthetic oil which has a saturated component of 85 wt.% or more (preferably 90 wt.% or more), a viscosity index of 110 or more (preferably 120 or more, more preferably 130 or more), and a sulfur content of 0.01 wt.% or less (preferably 0.001 wt.% or less).

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 120 or more, an evaporation loss (ASTM D5800) of 15 wt.% or less, a sulfur content of 0.01 wt.% or less, and an aromatic component content of 10 wt.% or less). In addition, an mineral oil mixture containing the hydrocracked oil in an amount of 10 wt.% or more. The hydrocracked oil includes a high viscosity index oil (such as having a viscosity index of 140 or more, specifically 140 to 150) which is obtained by subjecting mineral oil-origin slack wax or synthetic wax prepared from natural gas to isomerization and hydrocracking and a gas-to-liquid base oil. The hydrocracked oil has a low sulfur content and a low residual carbon content and shows a low evaporation property, and therefore is preferred for the use in the lubricating oil composition of the invention.

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.

Each of the mineral oil and synthetic oil can be employed singly. If desired, 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.

Metal-containing detergent

The lubricating oil composition of the invention contains as the metal-containing detergent an alkylsalicylate and/or an alkylcarboxylate of an alkali metal or an alkaline earth metal. The metal-containing detergent comprises an alkylsalicylate and/or an alkylcarboxylate of an alkali metal or an alkaline earth metal. Optionally, the alkylsalicylate and/or alkylcarboxylate may be employed in combination with a sulfonate and/or a phenate of an alkali metal or an alkaline earth metal.

In the lubricating oil composition of the invention, it is assumed that the alkylsalicylate and/or alkylcarboxylate of an alkali metal or an alkaline earth metal functions to increase dispersion of the soots and assists reduction of friction.

Preferred are an alkylsalicylate and an alkylcarboxylate of an alkaline earth metal. The alkaline earth metal preferably is calcium, barium, or magnesium. Calcium is most preferred.

The alkaline earth metal-containing salicylate generally is a an alkaline earth metal salt of an alkylsalicylic acid, which can be prepared from an alkylphenol by Kolbe-Schmidt reaction. The alkylphenol is obtained by a reaction of α-olefin having approx. 8 to 30 carbon atom (mean value) with phenol by Kolbe-Schmidt reaction. The alkaline earth metal salts can be ordinarily produced by subjecting their Na salt or K salt to double-decomposition or sulfuric acid decomposition, to give their Ca salt or Mg salt. The double decomposition using calcium chloride ($CaCl_2$) or the like is not preferred because chlorine is apt to migrate in the resulting product. Further, it is also known that an alkylphenol is directly neutralized to give its Ca salt, and then subjecting the Ca salt to a carbonation process to give the calcium salicylate. This process, however, gives the desired compound in a low yield, in comparison with the Kolbe-Schmidt reaction. Therefore, it is preferred to combine the Kolbe-Schmidt reaction and sulfuric acid decomposition. Preferred is a non-sulfurized alkyl-salicylate (alkaline earth metal salt) having a TBN in the range of 30 to 300 mg•KOH/g.

The alkaline earth metal carboxylate can be prepared, for instance, by neutralizing alkylphenol with an alkaline earth metal base in the presence of a carboxylic acid having 1 to 4 carbon atoms but in the absence of an alkali metal base, and carboxylating the resulting alkyl-phenate. The carboxylate can be a mono-aromatic ring hydrocarbylsalicylate-carboxylate which can be produced by treating an aromatic hydrocarbylsalicylate with a long chain carboxylic acid before, during, or after the aromatic hydrocarbylsalicylate is subjected to overbasing treatment. In these producing procedures, no Kolbe-Schmidt reaction (which includes production of an alkali metal salt) is performed. These producing procedures are described in Japanese Patent Provisional Publications

2000-63867 and 2000-87066.

Nitrogen-containing ashless dispersant

The nitrogen-containing ashless dispersant employed in the lubricating oil composition of the invention preferably has a weight average molecular weight or 4,500 to 20,000. The weight average molecular weight used in the specification is a molecular weight determined by GPC analysis using polystyrene as a reference compound.

Examples of the nitrogen-containing dispersants include alkenyl- or alkyl-succinimide or a derivative thereof which is derived from polyolefin. The nitrogen-containing dispersant is incorporated into the lubricating oil composition in an amount of 0.01 to 0.3 weight percent in terms of a nitrogen content, based on the total amount of the lubricating oil composition. A representative succinimide is obtained by the reaction between succinic anhydride having a substituent of an alkenyl group or an alkyl group which has a high molecular weight and polyalkylenepolyamine containing 4 to 10 nitrogen atoms (preferably 5 to 7 nitrogen atoms) per one molecule. The alkenyl group or an alkyl group which has a high molecular weight is preferably derived from polyolefin, particularly polybutene, having a number average molecular weight in the range of approx. 900 to 5,000.

The process for obtaining the polybutenyl-succinic acid 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 ppm) of chlorine. If the thermal reaction process using no chloride compound is employed, the reaction product contains only an extremely small chlorine (for instance, 40 ppm or less). Moreover, if a highly reactive polybutene (containing a methylvinylidene structure at least approx. 50%) is employed in place of the conventional polybutene (mainly containing a β-olefin structure), even the thermal reaction process can give a high reaction yield. If the reaction yield is high, the reaction product necessarily contains a reduced amount of the unreacted polybutene. This means that a dispersant containing a large amount of the effective component (succinimide) is obtained. Accordingly, it is preferred that the polybutenyl succinic acid anhydride is produced from the highly reactive polybutene by the thermal reaction and that the produced polybutenyl succinic acid anhydride is reacted with polyalkylenepolyamine having an average nitrogen atom number in the range of 4 to 10 (in one molecule) to give the succinimide. The succinimide further 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.

Other examples of the nitrogen-containing ashless dispersants include polymeric succinimide dispersants derived from ethylene-α-olefin copolymer (for instance, the molecular weight is 1,000 to 15,000), and alkenylbenzyl amine ashless dispersants.

In the lubricating oil composition of the invention, the nitrogen-containing ashless dispersant can be replaced with a nitrogen-containing dispersive viscosity index improver. As the nitrogen-containing dispersive viscosity index improver, a nitrogen-containing olefin copolymer or a nitrogen-containing polymethacrylate each having a weight mean molecular weight of 90,000 or more (in terms of polystyrene converted-molecular weight determined by GPC analysis). In consideration of thermal stability, the former is preferred.

The lubricating oil composition of the invention necessarily contains a nitrogen-containing ashless dispersant and/or a nitrogen-containing dispersive viscosity index improver. If desired, the other ashless dispersants such as an alkenylsuccinic acid ester dispersant can be employed in combination.

Neutral salt of fatty acid and fatty amine

The lubricating oil composition of the invention contains a neutral salt (or neutralized salt) of a fatty acid and a fatty amine as a friction modifier (friction reducing agent). The fatty acid preferably is a linear chain fatty acid having 8 to 30 carbon atoms. The fatty amine preferably is a linear chain fatty amine having 8 to 30 carbon atoms. It is preferred that the fatty group of one of the fatty acid and fatty amine is an unsaturated group (e.g., oleyl). It is also preferred that the fatty group of both of the fatty acid and fatty amine is an unsaturated group (e.g., oleyl). It is further preferred for the neutral salt of fatty acid and fatty amine that a difference between the acid value (unit: mg•KOH/g) and the amine value (unit: mg•KOH/g) is not more than 20, specifically not more than 15.

Examples of the preferred neutral salts of fatty acid and fatty amine include a salt of oleic acid with stearylamine, a salt of oleic acid with laurylamine, a salt of oleic acid with oleylamine, and a salt of a dioleic acid with N-oleylpropylenediamine. Both of the fatty acid and fatty amine can be employed their derivatives such as alkyleneoxide adducts or sulfides. Thus, the neutral acid salt of fatty acid and fatty amine according to the invention include salts of these derivatives.

Oxidation inhibitor

The oxidation inhibitor preferably is at least one oxidation inhibitor selected from the group consisting of the known phenolic oxidation inhibitor and the known amine oxidation inhibitor.

A representative phenolic oxidation inhibitor is a hindered phenol compound, and a representative amine oxidation inhibitor is a diarylamine compound.

The hindered phenol compound and diarylamine compound are advantageous because both further provide high detergency at a high temperature. The diarylamine oxidation inhibitor is particularly advantageous because it has a base number derived from the contained nitrogen which serves to increase detergency at a high temperature. In contrast, the hindered phenol oxidation inhibitor is effective to reduce oxidative deterioration caused by NO_x.

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-(5-t-butyl-4-hydroxy-3-methylphenyl)propionate.

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-β-naphthylamine, alkylated α-naphthylamine, and alkylated phenyl-α-naphthylamine.

Each of the hindered phenol oxidation inhibitor and diarylamine oxidation inhibitor can be employed singly or in combination. If desired, other oil soluble oxidation inhibitors can be employed in combination with the hindered phenol oxidation inhibitor and/or the diarylamine oxidation inhibitor.

<u>Other additives</u>

The lubricating oil composition of the invention can further contain a basic nitrogen-containing compound-oxymolybdenum complex. Preferred examples of the basic nitrogen-containing compound-oxymolybdenum complex include an oxymolybdenum complex of succinimide and an oxymolybdenum complex of carboxylamide.

The basic nitrogen-containing compound-oxymolybdenum complex can be prepared by the following process:

an acidic molybdenum compound or its salt is caused to react with a basic nitrogen-containing compound such as succinimide, carboxylamide, hydrocarbyl monoamine, hydrocarbyl polyamine, Mannich base, phosphonamide, thiophosphonamide, phosphoramide and a dispersant-type viscosity index improver (or a mixture thereof) at a temperature of 120°C or lower.

The lubricating oil composition of the invention may contain zinc dihydrocarbylditiophosphate or zinc dihydrocarbylphosphate both of which are known as multi-functional additives having an oxidation inhibition function and a friction reducing function. These additives can be incorporated into the lubricating oil composition in an amount of not more than 0.12 wt.% (in terms of phosphor content), preferably in the range of 0.01 to 0.12, more preferably in the range of 0.01 to 0.08.

As the zinc dihydrocarbyldithiophosphate, a zinc dialkyldithiophosphate having a primary or secondary alkyl group is used. From the viewpoint of anti-wear function, preferred is a zinc dialkyldithiophosphate having a secondary alkyl group which is derived from a secondary alcohol having 3 to 18 carbon atoms. In contrast, a zinc dialkyldithiophosphate having a primary alkyl group which is derived from a primary alcohol having 3 to 18 carbon atoms is advantageous in its excellent heat resistance and friction reducing function. The zinc dialkyldithiophosphate having a secondary alkyl group and the zinc dialkyldithiophosphate having a primary alkyl group can be used in combination. A zinc dialkyldithiophosphate having a primary alkyl group and a secondary alkyl group which can be obtained using a mixture of a primary alcohol and a secondary alcohol can also be favorably employed.

In addition, a zinc dialkylaryldithiophosphate (e.g., zinc dialkylaryldithiophosphate obtainable using dodecylphenol) can be employed.

A zinc dihydrocarbylphosphate can be employed in place of the zinc dihyrocarbyldithiophosphate. The former zinc dihydrocarbylphosphate may be advantageous from the viewpoint of minimizing sulfur content, because it contains no sulfur atoms.

In combination with the basic nitrogen-containing compound-oxymolybdenum complex, other molybdenum-containing compounds can be used. Examples of the molybdenum-containing compounds include sulfurized oxymolybdenum dithiocarbamate and sulfurized oxymolybdenum dithio-phosphate.

The lubricating oil composition of the invention may further contain an alkali metal borate hydrate for increasing stability at a high temperature and a basic number. The alkali metal borate hydrate can be contained in an amount of 5 wt.% or less, particularly 0.01 to 5 wt.%. Some alkali metal borate hydrates contain an ash component and a sulfur component. Therefore, the alkali metal borate hydrate can be used in an appropriate amount in consideration of the composition of the resulting lubricating oil composition.

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 polyisobutylene. A dispersant viscosity index improver and a multi-functional viscosity index improver which are produced by providing dispersant properties to the above-mentioned polymer are preferably employed. The viscosity index improvers can be used singly or in combination.

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:

zinc dithiocarbamate or methylenebis(dibutyl dithiocarbamate) as an oxidation inhibitor or a wear inhibitor; an oil soluble copper compound; sulfur compounds (e.g., olefin sulfide, sulfurized ester, and polysulfide); organic amide compounds (e.g., oleylamide), phosphor-containing esters (e.g., phosphoric acid ester, thiophosphoric acid ester, dithiophosphoric acid ester, and phosphorous acid ester); 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 anti-rust agent and anti-emulsifying agent; a variety of amines, amides, amine salts, their derivatives, aliphatic esters of polyhydric alcohols, and their derivatives which function as friction modifiers; and various compounds functioning as anti-foaming agents and pour point depressants.

The auxiliary additives can be preferably incorporated into the lubricating oil composition in an amount of 3 wt% or less (particularly, 0.001 to 3 wt.%).

The lubricating oil composition of the invention is preferably formulated to give a multi-grade engine oil of a relatively low viscosity, such as 0W20, 0W30, 0W40, 5W20, 5W30, 5W40, 10W20, or 10W30(SAE viscosity grade), by incorporating a viscosity index improver, from the viewpoint of fuel economy.

EXAMPLES

The invention is further illustrated by the following examples, which are not to be considered as limitative of its scope.

Example 1

(1) Preparation of lubricating oil composition

A lubricating oil composition of the invention having an SAE viscosity grade of 5W20 was prepared using the following additives and base oil.

(2) Additives:

-Nitrogen-containing ashless dispersant

1) Bis-succinimide dispersant-1 (weight average molecular weight: 12,800 (GPC analysis, value as molecular weight corresponding to polystyrene), nitrogen content: 1.0 wt.%, chlorine content: 30 wt.ppm., prepared by the steps of thermally reacting a highly reactive polyisobutene having a number average molecular weight of approx. 2,300 (containing at least approx. 50% of methylvinylidene structure) with maleic anhydride to give polyisobutenylsuccinic anhydride, reacting the polyisobutenylsuccinic anhydride with polyalkylenepolyamine having an average nitrogen atoms of 6.5 (per one molecule) to give a bis-succinimide, and reacting the bis-succinimide with ethylene carbonate): 0.05 wt.% (in terms of nitrogen content)

2) Bis-succinimide dispersant-2 (weight average molecular weight: 5,100, nitrogen content: 1.95 wt.%, boron content: 0.66 wt.%, chlorine content: less than 5 wt.ppm., prepared by the steps of thermally reacting a highly reactive polyisobutene having a number average molecular weight of approx. 1,300 (containing at least approx. 50% of methylvinylidene structure) with maleic anhydride to give polyisobutenylsuccinic anhydride, reacting the polyisobutenylsuccinic anhydride with polyalkylenepolyamine having an average nitrogen atoms of 6.5 (per one molecule) to give a bis-succinimide, and reacting the bis-succinimide with boric acid): 0.01 wt.% (in terms of nitrogen content)

-Alkaline earth metal-containing detergent

1) calcium salicylate (Ca: 6.3 wt.%, S: 0.1 wt.%, TBN: 177 mg•KOH/g): 0.23 wt.% (in terms of Ca content)

2) calcium salicylate (Ca: 11.4 wt.%, S: 0.2 wt.%, TBN: 320 mg•KOH/g): 0.008 wt.% (in terms of Ca content)

3) calcium sulfonate (Ca: 2.4 wt.%, S: 2.9 wt.%, TBN: 17 mg•KOH/g): 0.02 wt.% (in terms of Ca content)

-Oxidation inhibitor

1) Amine oxidation inhibitor (dialkyldiphenylamine having a mixture of C_4 and C_8 alkyl groups, N: 4.6 wt.%, TBN: 180 mg•KOH/g): 1.1 wt.%

2) Phenolic oxidation inhibitor (octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate): 0.2 wt.%

-Basic nitrogen-containing compound-oxymolybdenum complex

oxymolybdenum complex of succinimide (containing sulfur, Mo: 5.5 wt.%, S: 0.2 wt.%, N: 1.6 wt.%, TBN: 10 mg•KOH/g, OLOA 17502 available from Chevron Japan Co., Ltd.: 0.4 wt.%

-Zinc dithiophosphate

Zinc dialkyldithiophosphate (P: 7.2 wt.%, Zn: 7.8 wt.%, S: 14 wt.%, prepared by using a secondary alcohol having 3 to 8 carbon atoms: 0.077 wt.% (in terms of P content)

-Friction modifier

A salt of oleic acid and stearylamine (acid value: 98 mg•KOH/g, amine value: 108 mg•KOH/g): 0.6 wt.%

-Viscosity index improver

Non-dispersant ethylene-propylene copolymer viscosity index improver: 1.5 wt.%

-Pour point depressant

Polymethacrylate pour point depressant: 0.3 wt.%

(3) Base oil (residual amount)

Mixture of 50 weight parts of hydrocracked mineral oil-1 (kinematic viscosity at 100°C: 6.3 mm^2/s, viscosity index: 132, evaporation loss (ASTM D5800): 5.6 wt.%, sulfur content: less than 0.001 wt.%, saturated component content: 92 wt.%, aromatic component content: 8 wt.%) and 50 weight parts of hydrocracked mineral oil-2 (kinematic viscosity at 100°C: 4.1 mm^2/s, viscosity index: 127, evaporation loss (ASTM D5800): 14 wt.%, sulfur content:

less than 0.001 wt.%, saturated component content: 92 wt.%, aromatic component content: 8 wt.%)

Comparison Example 1

(1) Preparation of lubricating oil composition

The procedures of Example 1 were repeated except that the friction modifier is not used, to give a lubricating oil composition for comparison.

Comparison Example 2

(1) Preparation of lubricating oil composition

The procedures of Example 1 were repeated except that the friction modifier was replaced with the same amount (0.6 wt.%) of a fatty acid (oleic acid), to give a lubricating oil composition for comparison.

Comparison Example 3

(1) Preparation of lubricating oil composition

The procedures of Example 1 were repeated except that the friction modifier was replaced with the same amount (0.6 wt.%) of a fatty amine (stearyl amine), to give a lubricating oil composition for comparison.

Comparison Example 4

(1) Preparation of lubricating oil composition

The procedures of Example 1 were repeated except that the friction modifier was replaced with the same amount (0.6 wt.%) of a fatty acid ester (glycerol monooleate), to give a lubricating oil composition for comparison.

Comparison Example 5

(1) Preparation of lubricating oil composition

The procedures of Example 1 were repeated except that the friction modifier was replaced with the 1.1 wt.% of sulfurized oxymolybdenum dithiocarbamate (MoDTC, Mo: 4.5 wt.%, S: 4.7 wt.%), to give a lubricating oil composition for comparison.

Characteristics of lubrication oil compositions

The characteristics of the lubricating oil compositions obtained in Example 1 and Comparison Examples 1 to 5 are set forth in Table 1.

Table 1

	Example	Comparison Example				
	1	1	2	3	4	5
Sulfated ash	1.0	1.0	1.0	1.0	1.0	1.0
N	0.14	0.12	0.12	0.16	0.12	0.13
Ca	0.26	0.26	0.26	0.26	0.26	0.26
P	0.08	0.08	0.08	0.08	0.08	0.08
S	0.20	0.20	0.20	0.20	0.20	0.27
TBN	10.4	9.8	9.8	10.9	9.8	9.9

Remarks: Sulfated ash, N, Ca, P, S: wt.%
TBN (ASTM D-2896): mg•KOH/g

Evaluation of lubricating oil composition:

(1) HFRR Friction test (Friction test in the presence of dispersed carbon black)

In order to simulate soot emigration in a diesel engine oil, carbon black (mean particle diameter: 22 nm, specific surface area: 134 m^2/g, carbon particles produced by incomplete combustion of fuel) in an amount of 0 wt.%, 1 wt.%, or 2 wt.%) was blended in the lubricating oil composition by means of a high speed agitator to give a test oil. The test oil containing carbon black was then subjected to the HFRR test by means of a HFRR tester under the conditions of 105°C for oil temperature, 400 g of load, 1,000 μm for friction length, 20 Hz for frequency of reciprocating motion, and one hour for test period, to determine a friction coefficient. The results are set forth in Table 2.

(2) High temperature corrosion test (ASTM D6594)

The corrosion of non-iron metal by the diesel engine oil was evaluated. The test was carried out by introducing air into the test oil containing copper, lead, and phosphor bronze at 135°C (oil temperature) for 168 hours. The amount of copper, lead and tin having been dissolved in the test oil was measured. The test results and criteria are set forth in Table 2.

Table 2

	Example	Comparison Example				
	1	1	2	3	4	5
(1) HFRR Friction test						
Amount (wt.%) of Carbon black						

0	0.088	0.139	0.084	0.134	0.115	0.057
1	0.098	0.142	0.112	0.127	0.121	0.102
2	0.096	0.145	0.117	0.130	0.123	0.112

(2) High temperature corrosion test (ppm by weight)

Cu	18	-	4	44	-	-
Pb	54	-	401	43	-	-
Sn	0	-	0	0	-	-

Remarks:

Criteria for acceptable oil according to JASO M355:

Cu: ≤ 20, Pb: ≤ 100, Sn: ≤ 50

The results set forth in Tables 1 and 2 indicate that a lubricating oil composition of the invention containing a metal-containing detergent comprising an alkaline earth metal alkylsalicylate and a neutral salt of a fatty acid and a fatty amine shows satisfactory friction reduction regardless of a low sulfated ash content, a low sulfur content and a low phosphorus content even in the case that soots migrated into the lubricating oil composition.

WHAT IS CLAIMED IS:

1. A lubricating oil composition for lubricating internal combustion engines which has a sulfated ash content of 1.1 wt.% or less, a sulfur content of 0.5 wt.% or less, and a phosphorus content of 0.12 wt.% or less and which comprises a base oil having a lubricating viscosity and the following additive components:

a) a metal-containing detergent comprising at least one of an alkali metal or alkaline earth metal alkylsalicylate and an alkali metal or alkaline earth metal alkylcarboxylate in an amount of 0.01 to 0.4 wt.% in terms of an amount of metal contained in the composition;

b) at least one of a nitrogen-containing ashless dispersant and a nitrogen-containing dispersive viscosity index improver in an amount of 0.01 to 0.3 wt.% in terms of a nitrogen amount;

c) a neutral salt of a fatty acid having 8 to 30 carbon atoms with a fatty amine having 8 to 30 carbon atoms in an amount of 0.1 to 5 wt.%; and

d) an oxidation inhibitor in an amount of 0.1 to 5 wt.%.

2. The lubricating oil composition of claim 1, in which the fatty acid is an unsaturated fatty acid and the fatty amine is a saturated fatty amine.

3. The lubricating oil composition of claim 2, in which the fatty acid is an unsaturated linear chain fatty acid.

4. The lubricating oil composition of claim 3, in which the unsaturated linear chain fatty acid is oleic acid.

5. The lubricating oil composition of claim 2, in which the fatty amine is a saturated linear chain fatty amine.

6. The lubricating oil composition of claim 5, in which the saturated linear chain fatty amine is stearyl amine.

7. The lubricating oil composition of claim 1, in which the neutral salt of a fatty acid with a fatty amine is contained in an amount of 0.1 to 2 wt.%.

8. The lubricating oil composition of claim 1, in which the metal-containing detergent comprising at least one of an alkali metal or alkaline earth metal alkyl-salicylate and an alkali metal or alkaline earth metal alkylcarboxylate is contained in an amount of 0.1 to 0.4 wt.% in terms of an amount of metal contained in the composition.

9. The lubricating oil composition of claim 1, in which the base oil having a lubricating viscosity has a saturated component of 85 wt.% or more, a viscosity index of 110 or more, and a sulfur content of 0.01 wt.% or less.

10. The lubricating oil composition of claim 1, in which the nitrogen-containing ashless dispersant has a weight average molecular weight in the range of 4,500 to 20,000.

11. The lubricating oil composition of claim 1, which further comprises a zinc dihydrocarbyldithio-

phosphate or a zinc dihydrocarbylphosphate in an amount of 0.01 to 0.12 wt.% in terms of an amount of a phosphorus amount.

12. The lubricating oil composition of claim 1, which has a TBN in the range of 2 to 15 mg•KOH/g and is used for lubricating diesel engines.

13. A process for lubricating a diesel engine comprising operating the engine using the lubricating oil composition of claim 1.