

A METHOD OF IMPROVING THE ACRYLIC RUBBER SEALANT COMPATIBILITY IN AN INTERNAL COMBUSTION ENGINE

5 The present invention relates to a method of improving the acrylic rubber sealant compatibility in an internal combustion engine. More specifically, the present invention relates to a method comprising contacting acrylic rubber sealants in an internal combustion engine and operating the internal combustion engine with a lubricating oil composition having improved acrylic rubber sealant compatibility.

10 BACKGROUND OF THE INVENTION

In mechanical devices such as internal-combustion engine vehicles and various other industrial machines, it is necessary to supply a lubricating oil to mechanisms involving rubbing movement. Lubrication systems for supplying a lubricating oil are generally equipped with various sealing materials (sealants).
15 Examples of the sealing materials include resin or rubber sealants such as silicone rubber sealant, acrylic rubber sealant, fluorocarbon resin sealant, nitrile rubber sealant, hydrogenated nitrile rubber sealant and ethylene-propylene rubber sealant. According to their physical and chemical characteristics, those sealants are optionally selected to be installed in proper parts of the lubrication systems. Among the above-mentioned materials, acrylic rubber sealant is particularly used as packing parts for fixation because it is not only excellent in heat resistance and oil resistance but also inexpensive,

25 At the present time, it is required to improve lubricating oils for the purpose of meeting certain performance requirements. Most lubricating oils contacting rubbing mechanisms in various machines are nowadays high-performance lubricating oil compositions comprising a lubricating base oil and various additives added thereto.

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However, lubricating oil compositions containing various additives often deteriorate resin or rubber sealants despite satisfying lubricating performance requirements. Most of the additives contained in the compositions are so chemically active that they are liable to shrink the sealants and/or to impair their strength and elasticity.

Accordingly, it is desirable to have a lubricating oil composition which satisfies the severe performance requirements concerning lubricating oil compositions and, at the same time, which hardly impairs sealing performance of the sealants themselves.

U.S. Patent No. 6,124,247 describes a lubricating oil composition containing a borated glycerol ester and a mono-succinimide or bis-succinimide type dispersant subjected or not subjected to post-treatment with, for example, ethylene carbonate. It is stated that this oil composition has excellent compatibility with fluorocarbon elastomer, which is used as a sealant in a lubrication system of an internal-combustion engine.

JP-A-11-181461 describes that a lubricating oil composition containing an aliphatic amine has excellent compatibility with rubber sealants.

U.S. Patent No. 6,569,818 describes a lubricating oil composition containing an ashless dispersant of an alkenyl- or alkyl-succinic imide or a derivative thereof, an alkali metal or alkaline earth metal alkylsalicylate of non-sulfide or otherwise an alkali metal salt of alkylphenol derivative having a Mannich base structure, a zinc dialkyldithiophosphate, and an oxidation inhibiting phenol or amine compound. It is stated that all of the ash content, the phosphorus content and the sulfur content of the disclosed lubricating oil composition are low levels and that the lubricating oil composition gives high detergency at a high temperature. U.S. Patent No. 6,569,818, however, is silent about a lubricating oil composition of the present invention described hereinbelow. Further, this reference neither

describes nor suggests any effect that the lubricating oil composition has on sealants.

SUMMARY OF THE INVENTION

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The present invention relates to a method of improving acrylic rubber sealant compatibility in an internal combustion engine. The method involves contacting the acrylic rubber sealant in the internal combustion engine and operating the internal combustion engine with a lubricating oil composition comprising:

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- a) a major amount of a base oil of lubricating viscosity,
- b) a nitrogen-containing ashless dispersant in an amount of 0.01 to 0.3 wt.%, preferably 0.01 to 0.1 wt.%, in terms of the nitrogen content, based on the total amount of the lubricating oil composition,
- 15 c) a metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure in an amount of 0.001 to 0.4 wt.%, preferably 0.002 to 0.1 wt.%, in terms of the metal content, based on the total amount of the lubricating oil composition, and
- 20 d) a phosphorus-containing organic compound in an amount of 0.001 to 0.5 wt.%, preferably 0.01 to 0.2 wt.%, in terms of the phosphorus content, based on the total amount of the lubricating oil composition,

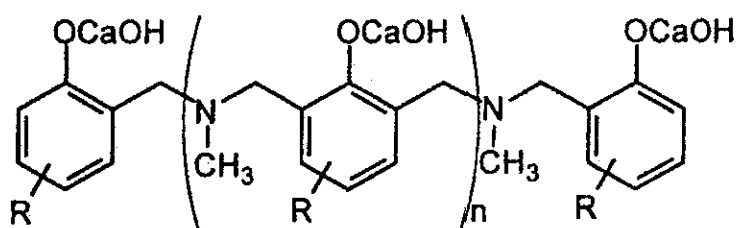
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wherein the ratio of components b) to c) is in the range of from 1:0.005 to 1:2, preferably 0:0.01 to 1:0.3, in terms of the nitrogen content.

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The nitrogen-containing ashless dispersant in the lubricating oil composition employed in the method of the present invention is an alkenyl- or alkyl-succinic imide or a derivative thereof.

The metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative in the lubricating oil composition employed in the method of the present invention has a Mannich base structure represented by the following formula:



wherein R is an alkyl group having 8 to 30 carbon atoms, and n is 0 or a positive integer.

The lubricating oil composition employed in the method of the present invention may further comprise a phosphorus-containing organic compound selected from the group consisting of zinc dihydrocarbyldithiophosphates, zinc dihydrocarbylphosphates, phosphoric acid esters, phosphorous acid esters, and thiophosphoric acid esters.

The lubricating oil composition employed in the method of the present invention may further comprise a metal-containing detergent selected from the group consisting of alkali metal or alkaline earth metal salicylates, carboxylates, phenates and sulfonates in an amount of 1.0 wt.% or less in terms of the metal content.

The amount of metal-containing detergent selected from the group consisting of alkali metal or alkaline earth metal salicylates, carboxylates, phenates and sulfonates to the amount of metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is in a ratio of 1:0.003 to 1:1 in terms of the metal content.

The lubricating oil composition employed in the method of the present invention may further comprise a molybdenum compound selected from the group consisting of an oxymolybdenum complex prepared by the reaction between an acidic molybdenum compound and a basic nitrogen compound, sulfurized
5 oxymolybdenum dithiocarbamate, and sulfurized oxymolybdenum dithiophosphate, in amount of 0.25 wt.% or less in terms of the molybdenum content.

The lubricating oil composition employed in the method of the present invention
10 may further comprise an alkali metal borate in an amount of 2 wt.% or less and an oxidation inhibitor selected from the group consisting of hindered phenol compounds and diarylamine compounds in an amount of 5 wt.% or less.

The base oil of lubricating viscosity contains 10 wt.% or more of a mineral oil
15 showing the following characteristics:

- 17 wt.% or less evaporation loss according to ASTM D-5800,
- 90 wt.% or more saturated content,
- 10 wt.% or less, aromatic component,
- 20 - 0.01 wt.% or less, sulfur content, and
- 120 or more viscosity index.

The lubricating oil composition employed in the method of the present invention is a SAE viscosity grade selected from the group consisting of 0W20, 0W30,
25 5W20, 5W30 and 10W30. Preferably, the lubricating oil composition meets the SAE 10W-30 viscosity grade.

Among other aspects, it has been discovered that a lubricating oil composition containing a certain combination of a nitrogen-containing dispersant and a metal-
30 containing detergent of an alkali metal salt of alkylphenol derivative having a Mannich base structure, together with a phosphorus-containing organic

compound, can be effectively employed in a method for improving the acrylic rubber sealant compatibility in an internal combustion engine, if the ratio of the nitrogen-containing dispersant and a metal-containing detergent of an alkali metal salt of alkylphenol derivative having a Mannich base structure is adjusted to a specific range, i.e., in the range of from 1:0.005 to 1:2 in terms of the nitrogen content. The lubricating oil composition hardly impairs the sealing performance of the acrylic rubber sealant.

DETAILED DESCRIPTION OF THE INVENTION

- The present invention resides in a method of employing a certain lubricating oil composition to improve the acrylic rubber sealant compatibility in an internal combustion engine. The lubricating oil composition, while meeting the lubricating performance requirements of internal combustion engines, at the same time is less detrimental to the sealing performance of acrylic rubber sealants found in internal combustion engines as compared to conventionally used lubricating oil compositions. Thus, the method of the present invention advantageously improves the acrylic rubber sealant compatibility in internal combustion engines.
- The preferred embodiments of the present invention will be described in further detail below. It should be noted that when weight percent is used herein, it is based on the total weight percent of the lubricating oil composition unless otherwise specified.
- The lubricating oil composition employed in the method of the present invention will contain a nitrogen-containing ashless dispersant. The nitrogen-containing ashless dispersant is preferably is a polyolefin-derived alkenyl- or alkyl-succinic imide or a derivative thereof. The amount of the nitrogen-containing ashless dispersant is in the range of 0.01 to 0.3 wt.%, preferably 0.01 to 0.1wt.%, in terms of the nitrogen content, based on the total amount of the lubricating oil composition.

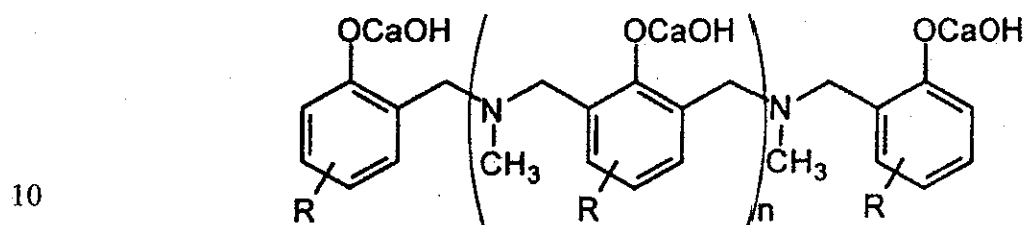
A representative succinic imide can be prepared by the reaction between succinic anhydride having a high molecular weight alkenyl or alkyl substituent group with polyalkylenepolyamine containing 4 to 10 nitrogen atoms on average, preferably 5 to 7 nitrogen atoms. The high molecular weight alkenyl or alkyl substituent group is preferably a polybutene having a number average molecular weight of approximately 900 to 5,000.

The process for preparing the polybutenylsuccinic anhydride by the reaction between polybutene and maleic anhydride is generally performed by a chlorination method utilizing chlorine. While this reaction is advantageous in giving a high reaction yield, it has a disadvantageous feature in that a large amount (for instance, approximately 2,000 to 3,000 ppm) of chlorine remains in the final succinic imide product. In contrast, a thermal reaction process utilizing no chlorine can give a final reaction product having an extremely low chlorine content (such as 0 to 30 ppm). It is, therefore, preferred to use a succinic imide derived from the polybutenylsuccinic anhydride prepared by the thermal reaction process so that the chlorine content can be in the range of 0 to 30 ppm. The resulting succinic imide can be further converted into a modified succinic imide by a further reaction with boric acid, alcohol, aldehyde, ketone, alkylphenol, cyclic carbonate or organic acids. From the thermal stability and oxidation stability, particularly preferred is a boron-containing alkenyl- or alkyl-succinic imide which is produced by the reaction with boric acid or a boron-containing compound.

The lubricating oil composition employed in the method of the present invention indispensably contains the ashless dispersant, whose representative example is an alkenyl- or alkyl-succinic imide or a derivative thereof. As the ashless dispersant, ashless dispersants of alkenylbenzylamine type and alkenylsuccinic acid ester type can be also used.

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The lubricating oil composition employed in the method of the present invention will contain metal-containing detergent of an alkali metal or alkaline metal earth metal salt of alkylphenol derivative. The metal-containing detergent of an alkali metal or alkaline metal earth metal salt of alkylphenol derivative has a Mannich base structure represented by the following formula:



The amount of the metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is in the range of 0.001 to 0.4 wt.% in terms of the metal content or 0.002 to 0.1 wt.% in terms of the nitrogen content, based on the total amount of the lubricating oil composition.

20 The metal-containing detergent of an alkali metal (e.g., sodium, potassium) or alkaline earth metal (e.g., calcium, barium, magnesium) salt of alkylphenol derivative having a Mannich base structure, is generally prepared by the steps of: synthesizing an intermediate having aminomethylated phenol ring by Mannich reaction from alkylphenol, formaldehyde, amine or an amine compound; and
25 neutralizing the synthesized intermediate with a base such as calcium hydroxide to convert it into a metal salt. Examples include the compound of the above formula having the following characteristics:

Ca content: 2.5 wt.%,
N content: 1.6 wt.%,
30 total base number: 135 mg•KOH/g, and

base number attributable to basic nitrogen: approximately 50% of the total base number.

5 The ratio of the nitrogen-containing ashless dispersant to the metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is in the range of from 1:0.005 to 1:2, preferably 1:0.01 to 1:0.3, in terms of the nitrogen content.

10 The lubricating oil composition employed in the method of the present invention will contain a phosphorus-containing organic compound selected from the group consisting of zinc dihydrocarbyldithiophosphates, zinc dihydrocarbylphosphates, phosphoric acid esters, phosphorous acid esters, and thiophosphoric acid esters. The amount of the phosphorus-containing organic compound is in the range of 0.001 to 0.5 wt.%, preferably 0.01 to 0.2 wt.%, in terms of the phosphorus
15 content, based on the total amount of the lubricating oil composition.

Examples of the phosphorus-containing organic compounds include zinc dihydrocarbyldithiophosphates, zinc dihydrocarbylphosphates, phosphoric acid esters, phosphorous acid esters, and thiophosphoric acid esters in which each
20 ester is generally derived from the corresponding acid and an alkylalcohol having 3 to 18 carbon atoms or an alkylarylalcohol having an alkyl group of 3 to 18 carbon atoms. If a zinc dihydrocarbyldithiophosphate (zinc dialkyldithiophosphate) is added, the amount of the additive is preferably in the range of 0.01 to 0.1 wt.% in terms of the phosphorus content, based on the total
25 amount of the lubricating oil composition. From the viewpoint of reducing the phosphorus content and the sulfur content, the amount preferably is in the range of 0.01 to 0.06 wt.%, based on the total amount of the lubricating oil composition.

30 The zinc dialkyldithiophosphate preferably has an alkyl group of 3 to 18 carbon atoms or an alkylaryl group having an alkyl group of 3 to 18 carbon atoms. It is particularly preferred for the zinc dialkyldithiophosphate to have an alkyl group

- derived from a secondary alcohol having 3 to 18 carbon atoms or an alkyl group derived from a mixture of a primary alcohol having 3 to 18 carbon atoms and a secondary alcohol having 3 to 18 carbon atoms, because the zinc dialkyldithiophosphate having that alkyl group is particularly effective in wear reduction. A zinc dialkyldithiophosphate derived from a primary alcohol is also excellent in heat resistance. The zinc dithiophosphates can be used singly, but it is preferred to use a mixture mainly comprising a secondary alkyl-type and/or a primary alkyl type.
- 10 The lubricating oil composition employed in the method of the present invention may further contain another metal-containing detergent selected from the group consisting of alkali metal or alkaline earth metal salicylates, carboxylates, phenates and sulfonates in an amount of 1.0 wt.% or less in terms of the metal content, based on the total amount of the lubricating oil composition.
- 15 The amount of the metal-containing detergent selected from the group consisting of alkali metal or alkaline earth metal salicylates, carboxylates, phenates and sulfonates to the amount of the metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is in a ratio of 1:0.003 to 1:1 in terms of the metal content, based on the total amount of the lubricating oil composition.
- 20 The lubricating oil composition employed in the method of the present invention may further contain an oxidation inhibitor selected from the group consisting of hindered phenol compounds and diarylamine compounds in an amount of 5 wt.% or less, based on the total amount of the lubricating oil composition. In view of having a base number attributable to nitrogen, diarylamine-type oxidation inhibitors are particularly advantageous. On the other hand, however, hindered phenol-type oxidation inhibitors effectively prevent deterioration caused by NO_x oxidation.
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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-thiodiethylenebis[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.

Examples of the diarylamine oxidation inhibitors include an alkyl diphenylamine containing a mixture of alkyl groups having 4 to 9 carbon atoms, p,p'-dioctyldiphenylamine, phenyl- α -naphthylamine, phenyl- α -naphthylamine, alkylated α -naphthylamine, and alkylated phenyl- α -naphthylamine.

Each of the hindered phenol compounds and the diarylamine compounds can be used singly or in combination. Other oil soluble oxidation inhibitors can be employed in combination.

The lubricating oil composition employed in the method of the present invention may further contain a molybdenum compound selected from the group consisting of an oxymolybdenum complex prepared by the reaction between an acidic molybdenum compound and a basic nitrogen compound, sulfurized oxymolybdenum dithiocarbamate, and sulfurized oxymolybdenum dithiophosphate, in an amount of 0.25 wt.% or less in terms of the molybdenum content, based on the total amount of the lubricating oil composition.

The molybdenum-containing compound mainly functions as a friction modifier, an oxidation inhibitor or an anti-wear agent in the lubricating oil composition employed in the method of the present invention. In addition, it also improves detergency at a high temperature. The molybdenum-containing compound is preferably in an amount of 10 to 2,500 ppm in terms of the molybdenum content. Examples of the molybdenum-containing compounds include sulfur-containing

molybdenum complex of succinimide, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum dithiophosphate, amine molybdenum complex compound, oxymolybdenum diethylate amide, and oxymolybdenum monoglyceride. Sulfur-containing molybdenum complex of succinimide is particularly effective in improving the detergency at a high temperature.

The lubricating oil composition employed in the method of the present invention may further contain an alkali metal borate in an amount of 2 wt.% or less, based on the total amount of the lubricating oil composition. The alkali metal borate hydrate is also effective in improving the detergency at a high temperature and in giving a base number. The term "alkali metal borate hydrate" in the present invention means a compound representatively prepared by the method disclosed in U.S. Patent Nos. 3,929,650 and 4,089,790. For example, it can be obtained by the steps of carbonating a neutral alkali metal or alkaline earth metal sulfonate in the presence of an alkali metal hydroxide to prepare a basic sulfonate; and making the basic sulfonate to react with boric acid, to prepare an alkali metal borate in the form of dispersed fine particles. The carbonation reaction is preferably conducted further in the presence of an ashless dispersant such as succinic imide. The alkali metal preferably is potassium or sodium. An example of the alkali metal borate hydrate additive is a suspension comprising a mixture of neutral calcium sulfonate and succinic imide and fine particles of $\text{KB}_3\text{O}_5 \cdot \text{H}_2\text{O}$ having sizes of approximately 0.3 μm or less. The potassium can be replaced with sodium. The additive is also preferably used in consideration of water resistance.

The lubricating oil composition employed in the method of the present invention may further contain a viscosity index improver in an amount of 20 wt.% or less, preferably 1 to 20 wt.%, based on the total amount of the lubricating oil composition. Examples of the viscosity index improver include polymer compounds such as polyalkyl methacrylate, ethylene-propylene copolymer,

styrene-butadiene copolymer, and polyisoprene. Also employable are dispersant-type viscosity index improvers, which can be obtained by modifying the above polymers so that they can function as dispersants, and multi-functional viscosity index improvers. The viscosity index improvers can be used singly or in
5 combination.

The lubricating oil composition employed in the method of the present invention may further contain various other auxiliary additives. Examples of the auxiliary additives include zinc dithiocarbamate, methylenebis(dibutyldithiocarbamate), an
10 oil-soluble copper compound, a sulfur-containing compound (e.g., sulfurized olefin, sulfurized ester, polysulfide), and an organic amide compound (e.g., oleyl amide). They function as oxidation inhibitors or anti-wear agents. It is also preferred to incorporate metal deactivators such as benzotriazole compounds and thiadiazole compounds. Further, a nonionic surface active agent of
15 polyoxyalkylene such as a copolymer of polyoxyethylenealkylphenyl ether, ethylene oxide and propylene oxide can be added as a rust preventing agent or an demulsifier. It is also possible to incorporate various amines, amides, amine salts or derivatives thereof, and aliphatic acid esters of polyhydric alcohols or their derivatives. They serve as friction modifiers. It is further possible to
20 incorporate various compounds that function as defoaming agents or pour point depressants. Each auxiliary additive is added to the lubricating oil composition employed in the method of the present invention preferably in an amount of 3 wt.% or less, preferably 0.001 to 3 wt.% , based on the total amount of the lubricating oil composition.

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Base Oil of Lubricating Viscosity

The base oil used in the lubricating oil composition employed in the method of the present invention generally is a mineral or synthetic oil showing a kinematic
30 viscosity of 2 to 50 mm²/s at 100°C. There are no specific conditions with respect to the mineral or synthetic oil, but the base oil has a sulfur content of preferably

0.1 wt.% or less, more preferably 0.03 wt.% or less, most preferably 0.005 wt.% or less.

5 The mineral base oil is preferably subjected to properly combined treatments. For example, the mineral lubricant distillate thereof is preferably subjected to treatments such as solvent refining and hydrogenation processing in combination. In the present invention, it is preferred to use a highly hydrogen-refined (hydrocracked) base oil (having, for example, a viscosity index of 100 to 150, an aromatic component content of 5 wt.% or less, a nitrogen content of 50
10 ppm or less, and a sulfur content of 50 ppm or less). Examples include a high viscosity index-base oil prepared by isomerization or hydrocracking of synthetic wax synthesized from slack wax (crude wax) of mineral oil or natural gas.

15 It is particularly preferred that the base oil of lubricating viscosity is a mineral oil showing the following characteristics:

evaporation loss (ASTM D-5800): 17 wt.% or less,
content of saturated component: 90 wt.% or more,
content of aromatic component: 10 wt.% or less,
sulfur content: 0.01 wt.% or less, and
20 viscosity index: 120 or more;

or otherwise that the base oil of lubricating viscosity is a mineral oil mixture containing 10 wt.% or more of the above-mentioned mineral oil.

Examples of the synthetic oils (synthetic lubricant base oil) include a poly- α -olefin (copolymer of α -olefin having 3 to 12 carbon atoms), a dialkyl diester (ester
25 derived from an alcohol having 4 to 18 carbon atoms and a dibasic acid such as adipic acid, azelaic acid or sebacic acid) such as dioctyl sebacate, a polyol ester (ester derived from a monobasic acid having 3 to 18 carbon atoms and 1-trimethylolpropane or pentaerythritol), and an alkylbenzene having an alkyl group of 9 to 40 carbon atoms.

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Any of the above mineral or synthetic base oils may be used singly, but two or more of the mineral base oils or two or more of the synthetic base oils can be used in combination, if desired. Further, the mineral and synthetic base oils can be used in combination at any ratios, if desired, to prepare the appropriate base oil of lubricating viscosity.

It is preferred to use a major amount of base oil of lubricating viscosity in the lubricating oil composition employed in the method of the present invention. A major amount of base oil of lubricating viscosity as defined herein comprises 40 wt % or more. Preferred amounts of base oil comprise 40 to 99.9 wt %, preferably greater than 50 to 97 wt %, more preferably 60 to 97 wt % of the lubricating oil composition.

The lubricating oil composition employed in the method of the present invention can be prepared by adding the additives independently or all at once to the base oil. Otherwise, an additive concentrate comprising the additives in high concentrations can be beforehand prepared and then mixed it with a base oil to prepare the lubricating oil composition employed in the method of the present invention.

EXAMPLES

The base oil of lubricating viscosity and the additives used in the below-described Examples and Comparative Example are as follows:

(1) Base oil of lubricating viscosity

Solvent refined base oil (A) (kinematic viscosity: 4.9 mm²/s at 100°C, viscosity index: 103, evaporation loss (ASTM D5800): 13 wt.%, sulfur content: 0.19 wt.%, content of saturated component: 70 wt.%) and solvent refined base oil (B) (kinematic viscosity: 10.8 mm²/s at 100°C, viscosity index: 97, evaporation loss

(ASTM D5800): 2.3 wt.%, sulfur content: 0.22 wt.%, content of saturated component: 68 wt.%) were mixed in the ratio of 88:12 by weight to use.

(2) Additives

5 Dispersant A: ethylene carbonate-treated succinimide dispersant [N content: 1.0 wt.%, Cl content: 30 ppm by weight] which was prepared by the steps of:

- 10 a) reacting a polybutene having a number average molecular weight of approximately 2,300 and 50% or more of methylvinylidene structure with maleic anhydride according to the thermal process, to produce an intermediate product;
- b) reacting the intermediate product with a polyalkylenepolyamine containing 6.5 nitrogen atoms (in one molecule) on average, to prepare succinimide of bis-form; and then
- 15 c) treating the succinimide of bis-form with ethylene carbonate.

 Dispersant B: boron-containing succinimide dispersant [N content: 1.95 wt.%, B content: 0.66 wt.%, Cl content: less than 5 ppm by weight] which was prepared by the steps of:

- 20 a) reacting a polybutene having a number average molecular weight of approximately 1,300 and 50% or more of methylvinylidene structure) with maleic anhydride according to the thermal process, to produce an intermediate product;
- b) reacting the intermediate product with a polyalkylenepolyamine
- 25 containing 6.5 nitrogen atoms (in one molecule) on average, to prepare succinimide of bis-form; and then
- c) treating the succinimide of bis-form with boric acid.

30 Detergent A: Mannich base calcium phenate (Ca: 2.5 wt.%, N: 1.6 wt.%, S: 0.1 wt.%, TBN: 135 mg•KOH/g).

Detergent B: overbased sulfurized calcium phenate (Ca: 9.25 wt.%, S: 3.4 wt.%, TBN: 255 mg•KOH/g).

5 Detergent C: overbased calcium sulfonate (Ca: 16.1 wt.%, TBN: 425 mg•KOH/g).

Detergent D: basic calcium sulfonate (Ca: 2.35 wt.%, TBN: 17 mg•KOH/g).

10 ZnDTP-1: zinc dialkyldithiophosphate (P: 7.2 wt.%, Zn: 7.85 wt.%, S: 14.4 wt.%, starting material: a secondary alcohol having 3 to 6 carbon atoms).

ZnDTP-2: zinc dialkyldithiophosphate (P: 7.3 wt.%, Zn: 8.4 wt.%, S: 14 wt.%, starting material: a primary alcohol having 8 carbon atoms).

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Oxidation inhibitor: dialkyldiphenylamine (alkyl group: mixture of C₄-alkyl and C₈-alkyl groups, N: 4.6 wt.%, TBN: 180 mg•KOH/g).

20 Mo compound: sulfur-containing molybdenum-succinimide complex (Mo: 5.5 wt.%, S: 0.2 wt.%, N: 1.6 wt.%, TBN: 10 mg•KOH/g).

Alkali metal borate: dispersed fine particles of potassium borate hydrate (K: 8.3 wt.%, B: 6.8 wt.%, S: 0.26 wt.%, TBN: 125 mg•KOH/g).

25 Viscosity index improver (VII): ethylenepropylene copolymer of non-dispersant type.

Pour point depressant (PPD): polymethacrylic compound.

Example 1

The below-mentioned additives and the base oil of lubricating viscosity were
5 mixed to give the lubricating oil composition employed in the method of the
present invention. The lubricating oil composition was SAE viscosity grade
10W30. Also shown below are the contents of each element (Ca, P, N) in the
lubricating oil composition, the ratio between the nitrogen content attributable to
10 all the dispersants and that attributable to the detergent A (Mannich base calcium
phenate), and the ratio between the metal content attributable to all the
detergents and that attributable to the detergent A (Mannich base calcium
phenate).

(1) Additives

15 Dispersant A (amount: 3.0 wt.%, content in terms of nitrogen: 0.03 wt.%),
Dispersant B (amount: 1.5 wt.%, content in terms of nitrogen: 0.03 wt.%),
Detergent A (amount: 0.4 wt.%, content in terms of calcium: 0.01 wt.%,
content in terms of nitrogen: 0.006 wt.%),
Detergent B (amount: 0.86 wt.%, content in terms of calcium: 0.08 wt.%),
20 Detergent C (amount: 0.87 wt.%, content in terms of calcium: 0.14 wt.%),
Detergent D (amount: 0.43 wt.%, content in terms of calcium: 0.01 wt.%),
ZnDTP-1 (amount: 0.97 wt.%, content in terms of phosphorus: 0.07 wt.%),
ZnDTP-2 (amount: 0.41 wt.%, content in terms of phosphorus: 0.03 wt.%),
Oxidation inhibitor (amount: 0.2 wt.%),
25 Mo compound (amount: 0.15 wt.%, content in terms of molybdenum: 83
ppm by weight),
Alkali metal borate (amount: 0.25 wt.%),
Viscosity index improver (VII, amount: 6.3 wt.%), and
Pour point depressant (PPD, amount: 0.3 wt.%).

30 (2) Base oil of lubricating viscosity (amount: residual amount)

(3) Content of each element (Ca, P, N) in the lubricating oil composition

Calcium (Ca): 0.24 wt.%, Phosphorus (P): 0.10 wt.%, Nitrogen (N): 0.08 wt.%

(4) Ratio of the nitrogen content attributable to all the dispersants to that attributable to the detergent A (Mannich base calcium phenate): 1:0.1

5 (5) Ratio of the metal content attributable to all the detergents in the composition to that attributable to the detergent A (Mannich base calcium phenate): 1:0.04

Example 2

10 The procedures of Example 1 were repeated except for changing the amount of the detergent A (Mannich base calcium phenate) into 1.16 wt.% (content in terms of calcium: 0.03 wt.%, content in terms of nitrogen: 0.018 wt.%) and for changing the residual amount of the base oil of lubricating viscosity so that the total amount of the lubricating oil composition is 100 wt.%. The prepared lubricating oil
15 composition was SAE viscosity grade 10W30. Shown below are the contents of each element (Ca, P, N) in the lubricating oil composition, a ratio between the nitrogen content attributable to all the dispersants and that attributable to the detergent A (Mannich base calcium phenate), and a ratio between the metal content attributable to all the detergents and that attributable to the detergent A
20 (Mannich base calcium phenate).

(1) Contents of each element (Ca, P, N) in the lubricating oil composition

Calcium (Ca): 0.26 wt.%, Phosphorus (P): 0.10 wt.%, Nitrogen (N): 0.09 wt.%

25 (2) Ratio of the nitrogen content attributable to all the dispersants to that attributable to the detergent A (Mannich base calcium phenate): 1:0.3

(3) Ratio of the metal content attributable to all the detergents in the lubricating oil composition to that attributable to the detergent A (Mannich base calcium phenate): 1:0.12

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Comparative Example A

Comparative Example A was prepared according to the procedures of Example 1 except for not adding the detergent A (Mannich base calcium phenate) and for changing the amount of the base oil of lubricating viscosity so that the total amount of the lubricating oil composition is 100 wt.%. The prepared lubricating oil composition was SAE viscosity grade 10W30. The contents of each element (Ca, P, N) in the lubricating oil composition are shown below.

(1) Contents of each element (Ca, P, N) in the lubricating oil composition

Calcium (Ca): 0.23 wt.%, Phosphorus (P): 0.10 wt.%, Nitrogen (N): 0.07 wt.%

Evaluation of Compatibility With Acrylic Rubber Sealant

According to the affinity test for sealing rubber (CEC-L-39-T-96), compatibility with acrylic rubber was evaluated in the following manner. A piece of RE2-99 (acrylic rubber) was immersed in the lubricating oil composition to be tested at 150°C for 7 days, and then the degree of deterioration of the acrylic rubber piece was evaluated. The results are set forth in Table 1. In Table 1, the pass limits specified in JASO (Japanese Automobile Standard Organization) M355-2005 are also shown.

Table 1.

	Pass Limit	Example 1	Example 2	Comparative Example A
Volume change(%)	-7 to +5	+2	0	+2
Hardness change	-5 to +8	+3	+4	+3
Tensile strength change (%)	-15 to +18	+2	+2	-4
Elongation change(%)	-35 to +10	-23	-19	-35

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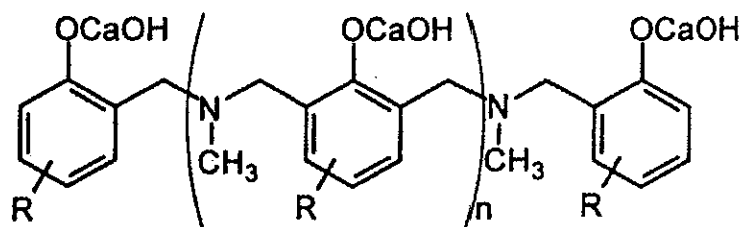
The above results shown in Table 1 indicate that both the lubricating oil compositions of the present invention (Examples 1 and 2) and that for Comparative Example A satisfy the JASO standards. It is also shown that the lubricating oil compositions of the present invention were remarkably improved in the elongation change, as compared with the lubricating oil composition for comparative example.

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Claims:

1. A method of improving the acrylic rubber sealant compatibility in an internal combustion engine, said method comprising contacting the acrylic rubber sealant in the internal combustion engine and operating the internal combustion engine with a lubricating oil composition comprising:
- a) a major amount of a base oil of lubricating viscosity,
- b) a nitrogen-containing ashless dispersant in an amount of 0.01 to 0.3 wt.% in terms of the nitrogen content, based on the total amount of the lubricating oil composition,
- c) a metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure in an amount of 0.001 to 0.4 wt.% in terms of the metal content, based on the total amount of the lubricating oil composition, and
- d) a phosphorus-containing organic compound in an amount of 0.001 to 0.5 wt.% in terms of the phosphorus content, based on the total amount of the lubricating oil composition,
- wherein the ratio of components b) to c) is in the range of from 1:0.005 to 1:2 in terms of the nitrogen content.
2. The method according to claim 1, wherein the nitrogen-containing ashless dispersant is an alkenyl- or alkyl-succinic imide or a derivative thereof.
3. The method according to claim 1 or claim 2, wherein the metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is represented by the following formula:

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wherein R is an alkyl group having 8 to 30 carbon atoms, and n is 0 or a positive integer.

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4. The method according to any one of the preceding claims, wherein the phosphorus-containing organic compound is selected from the group consisting of zinc dihydrocarbyldithiophosphates, zinc dihydrocarbylphosphates, phosphoric acid esters, phosphorous acid esters, and thiophosphoric acid esters.

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5. The method according to any one of the preceding claims, wherein the amount of the nitrogen-containing ashless dispersant is in the range of 0.01 to 0.1 wt.% in terms of the nitrogen content, based on the total amount of the lubricating oil composition.

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6. The method according to any one of the preceding claims, wherein the amount of the metal-containing detergent of an alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is in the range of 0.002 to 0.1 wt.% in terms of the nitrogen content, based on the total amount of the lubricating oil composition.

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7. The method according to any one of the preceding claims, wherein the amount of the phosphorus-containing organic compound is in the

range of 0.01 to 0.2 wt.% in terms of the phosphorus content, based on the total amount of the lubricating oil composition.

- 5 8. The method according to any one of the preceding claims, further comprising a metal-containing detergent selected from the group consisting of alkali metal or alkaline earth metal salicylates, carboxylates, phenates and sulfonates in an amount of 1.0 wt.% or less in terms of the metal content, based on the total amount of the lubricating oil composition.
- 10 9. The method according to claim 8, wherein the amount of metal-containing detergent selected from the group consisting of alkali metal or alkaline earth metal salicylates, carboxylates, phenates and sulfonates and the amount of the metal-containing detergent of an
- 15 alkali metal or alkaline earth metal salt of alkylphenol derivative having a Mannich base structure is in a ratio of 1:0.003 to 1:1 in terms of the metal content.
- 20 10. The method according to any one of the preceding claims, further comprising a molybdenum compound selected from the group consisting of an oxymolybdenum complex prepared by the reaction between an acidic molybdenum compound and a basic nitrogen compound, sulfurized oxymolybdenum dithiocarbamate, and sulfurized
- 25 oxymolybdenum dithiophosphate, in amount of 0.25 wt.% or less in terms of the molybdenum content, based on the total amount of the lubricating oil composition.
- 30 11. The method according to any one of the preceding claims, further comprising an alkali metal borate in an amount of 2 wt.% or less, based on the total amount of the lubricating oil composition.

5 12. The method according to any one of the preceding claims, further comprising an oxidation inhibitor selected from the group consisting of hindered phenol compounds and diarylamine compounds in an amount of 5 wt.% or less, based on the total amount of the lubricating oil composition.

10 13. The method according to any one of the preceding claims, wherein the base oil contains 10 wt.% or more of a mineral oil showing the following characteristics:

- 17 wt.% or less evaporation loss according to ASTM D-5800,
- 90 wt.% or more saturated content,
- 10 wt.% or less, aromatic component,
- 0.01 wt.% or less, sulfur content, and
- 15 - 120 or more viscosity index.

20 14. The method according to any one of the preceding claims, wherein the lubricating oil composition is a SAE viscosity grade selected from the group consisting of 0W20, 0W30, 5W20, 5W30 and 10W30.

15. The method according to claim 14, wherein the lubricating oil composition is a SAE viscosity grade selected from the group consisting of 10W30.