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Lubricating oil composition

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ABSTRACT

LUBRICATING OIL COMPOSITION

The present invention is a lubricating oil, especially a lubricating oil for internal combustion engines, which has friction-reducing properties even under sliding conditions varying substantially in internal combustion engines and the like and which can retain friction-reducing properties over an extend even in the presence of nitrogen oxide gas. The lubricating oil composition contains a lubricating base oil, and an organomolybdenum compound, an organomono-sulfide compound, and an organopolysulfide compound.

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AUSTRALIA

Patents Act 1990

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:
Lodged:

Invention Title: LUBRICATING OIL COMPOSITION

The following statement is a full description of this invention, including the best method of performing it known to us :-

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a lubricating oil composition, more specifically to a lubricating oil composition having excellent friction-reducing properties under diverse sliding conditions and permitting retention of such friction-reducing properties over an extended time even in the presence of nitrogen oxide gas, and especially to a lubricating oil composition suitable as a lubricating oil for internal combustion engines.

DESCRIPTION OF THE RELATED ART

In powertrain equipments such as internal combustion engines, automatic transmissions, shock absorbers and power steering systems, lubricating oil is used to smooth their operations. In particular, lubricating oil for an internal combustion engine is required to provide smooth lubrication primarily on various sliding surfaces of different conditions of piston rings, cylinder liners, bearings for a crankshaft and a connecting rod, valve-operating mechanisms including cams and valve lifters, and the like. As a lubricating oil for an internal combustion engine, it is considered essential to have friction-reducing properties under diverse sliding conditions.

Moreover, keeping in step with the recent move toward internal combustion engines of higher performances, such as higher gas mileage and higher power output, and more severe operating conditions, there is an increasing demand for higher lubricating performance. On the other hand, if combustion gas leaks even partly as blowby gas into a crankcase from between a piston and a cylinder in an internal combustion engine, nitrogen oxide gas which is contained at a substantially high concentration in the combustion gas together with oxygen in the blowby gas, deteriorates a lubricating oil for the internal combustion engine. Because of the move toward internal combustion engines of higher performance in recent years, combustion gas which leaks into a crankcase tends to contain nitrogen oxide gas at a higher concentration. It is therefore extremely important for an internal combustion engine lubricating oil to provide a low coefficient of friction under diverse sliding conditions and moreover, to retain such a low coefficient of friction over an extend time.

As a substantial energy loss takes place at each lubricated friction part in an internal combustion engine, a friction modifier has conventionally been added to a lubricating oil as a measure for reducing the friction loss and improving the gas mileage. As illustrative friction modifiers, organomolybdenum compounds, fatty acid esters, alkylamines and the like are used in general. For an illustrative lubricating oil composition making use of an organomolybdenum compound, reference may be had, for example, to Japanese Patent Application Laid-Open (Kokai) No. SHO 59-122597. According to this publication, a lubricating oil composition making combined use of (a) molybdenum oxysulfide organophosphorothioate and/or molybdenum dithiocarbamate and (b) zinc dithiophosphate is proposed. The lubricating oil composition disclosed in the publications has a low coefficient of friction and exhibits friction-reducing effects in an initial stage of its use, but involves a drawback that its effects can hardly be retained in its use over an extended time, especially in the presence of nitrogen oxide gas.

On the other hand, Japanese Patent Application Laid-Open (Kokai) No. HEI 8-73878 discloses an engine oil composition making combined use of

(a) molybdenum dithiocarbamate and (b) zinc dithiophosphate and further (c) an ashless organopolysulfide while claiming that it can retain a low coefficient of friction over an extended time. Nonetheless, this lubricating oil composition is accompanied by a problem that the coefficient of friction becomes higher in a low sliding speed range under reciprocating friction. It is therefore not considered to have quality sufficient for application under various conditions as a lubricating oil for an automotive internal combustion engine in which sliding conditions vary substantially.

In view of the above-described situations of lubricating oils of friction-reducing properties developed to date, the present invention has as an object thereof the provision of a lubricating oil composition which can maintain friction-reducing properties even when sliding conditions vary substantially in an internal combustion engine and which can retain such friction-reducing properties over an extended time, especially even in the presence of nitrogen oxide gas.

To solve the above-described problems, the present inventors have proceeded with extensive research. As a result, it has been found that a combination of an organomonosulfide compound and an organopolysulfide with an organomolybdenum compound makes it possible to provide low coefficients of friction under diverse sliding conditions and further to retain friction-reducing properties in application over an extended time. These findings have now led to the completion of the present invention.

DESCRIPTION OF THE FIGURE

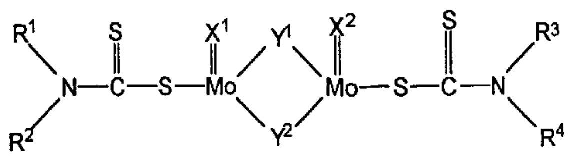
Figure 1 is a basic schematic diagram of a friction tester employed for the measurement of coefficients of friction of lubricating oil compositions according to the present invention.

DESCRIPTION OF THE INVENTION

The present invention relates to a lubricating oil composition comprising: a lubricating base oil, and an organomolybdenum compound in a proportion of from 100 to 2,000 ppm in terms of molybdenum (Mo) content, an organomonosulfide compound in a proportion of from 80 to 2,000 ppm in terms of sulfur (S) content, and an organopolysulfide compound in a proportion of from 80 to 1,500 ppm in terms of sulfur (S) content.

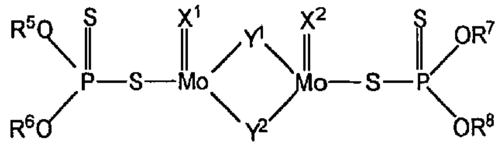
As preferred embodiments of the present invention, the present invention can provide lubricating compositions obtained by using a mineral oil and/or a synthetic oil as a lubricating base oil and adding thereto the following:

(a) 100 to 2,000 ppm, in terms of molybdenum (Mo) content, of an organo-molybdenum compound represented by the following formula [I]:



[I]

and/or the following formula [II]:



[II]

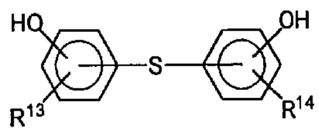
wherein R^1 to R^8 are hydrocarbon groups, and X^1, X^2, Y^1 and Y^2 are oxygen atoms or sulfur atoms;

(b) 100 to 1,800 ppm, in terms of sulfur (S) content, of an organomonosulfide compound represented by any one of the following formulas [III] to [VI]:

$$R^9—S—R^{10} \quad [III]$$

$$OHC—R^{11}—S—R^{12}—CHO \quad [IV]$$

$$R^9OOC—R^{11}—S—R^{12}—COOR^{10} \quad [V]$$



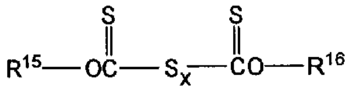
[VI]

and,

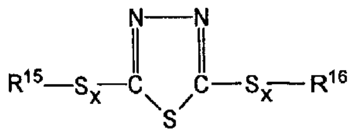
(c) 100 to 1,200 ppm, in terms of sulfur (S) content, of at least one organopolysulfide compound selected from those represented by the following formulas [VII] to [XII]:

$$R^{15}—S_x—R^{16} \quad [VII]$$

$$R^{15}OOC—R^{17}—S_x—R^{18}—COOR^{16} \quad [VIII]$$

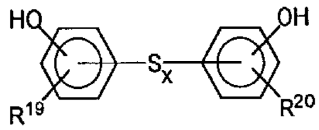


[IX]



[X]

$OHC—R^{17}—S_x—R^{18}—CHO$ [XI]



[XII]

wherein R^9 to R^{20} are hydrocarbon groups, and x stands for an integer of at least 2.

The present invention will hereinafter be described in detail.

No particular limitation is imposed on the lubricating base oil for use in the lubricating oil composition according to the present invention. Any one of those conventionally employed as base oils in lubrication oils, for example, any one of mineral-oil-type base oils, synthetic base oils and mixed base oils thereof can be used. Usable examples of such mineral-oil-type base oils include mineral oils obtained by treating lubricating oil fractions, which are available by vacuum distillation of atmospheric distillation residues of paraffin, neutral or naphthene crude oils, to one or more refining steps such as solvent refining, hydrogenation,

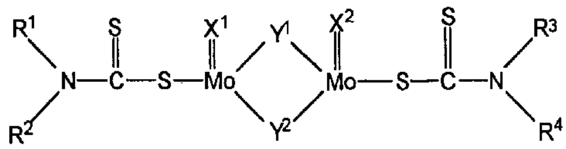
hydrogenation refining, catalytic dewaxing, solvent dewaxing, clay treatment and/or the like; mineral oils obtained by subjecting vacuum distillation residues to solvent deasphalting and then treating the deasphalted oils through one or more of the above-described refining steps; mineral oils available by isomerization of wax components; and mixed oils thereof. In the above-described solvent refining, an aromatic extraction solvent such as phenol, furfural or N-methylpyrrolidone is used, and as a solvent for solvent dewaxing, propane, MEK/toluene or the like is employed.

On the other hand, illustrative of such synthetic base oils are poly(α-olefin) oligomers, polybutene, alkylbenzenes, polyol esters such as trimethylolpropane esters and pentaerythritol esters, polyoxyalkylene glycols, polyoxyalkylene glycol esters, polyoxyalkylene glycol ethers, dibasic acid esters, phosphate esters, and silicone oils. These base oils can be used either singly or in combination.

As base oils for use in the lubrication oil composition according to the present invention, those having a viscosity in a range of from 3 mm^2/s to 20 mm^2/s at 100°C are preferred. Particularly preferred are hydrocracked oils and wax-isomerized oils, which contain 3 wt% or less of aromatic components (% C_A) and have a sulfur content of 50 ppm or less and a nitrogen content of 50 ppm or less.

Examples of the organomolybdenum compound added as a friction modifier in the lubricating oil composition according to the present invention include:

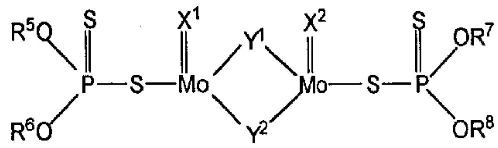
molybdenum oxysulfide dithiocarbamates (which may be abbreviated as "MoDTC's") represented by the following formula [I]:



[I]

and

molybdenum oxysulfide phosphorothioates (which may be abbreviated as "MoDTP's") represented by the following formula [II]:



[II]

In the above formulas [I] and [II], R^1 to R^8 may be the same or different and are hydrocarbon groups having 1-30 carbon groups. Illustrative of the hydrocarbon groups are linear or branched alkyl groups having 1-30 carbon atoms; alkenyl groups having 2-30 carbon atoms; cycloalkyl groups having 4-30 carbon atoms; aryl groups, alkylaryl group and arylalkyl groups having 6 to 30 carbon groups. In particular, alkyl groups having 3-20 carbon atoms are preferred. Examples include propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups, and their corresponding branched alkyl groups. Alkyl groups having 4-18 carbon atoms are particularly preferred. Further, alkenyl groups having 4-18 carbon atoms can also be employed. X^1 and X^2 are oxygen atoms or sulfur atoms, and Y^1 and Y^2 are oxygen atoms or sulfur atoms.

Accordingly, representative examples of the molybdenum oxysulfide dithiocarbamates represented by the formula [I] are molybdenum oxysulfide propyldithiocarbamate, molybdenum oxysulfide isopropyldithiocarbamate, molybdenum oxysulfide isobutyldithiocarbamate, molybdenum oxysulfide pentyldithiocarbamate, molybdenum oxysulfide isopentyldithiocarbamate, molybdenum oxysulfide hexyldithiocarbamate, molybdenum oxysulfide 2-ethylbutyldithiocarbamate, molybdenum oxysulfide heptyldithiocarbamate, molybdenum oxysulfide octyldithiocarbamate, molybdenum oxysulfide 2-ethylhexyldithiocarbamate, molybdenum oxysulfide 2-propylpentyldithiocarbamate, molybdenum oxysulfide nonyldithiocarbamate, molybdenum oxysulfide 2-propylhexyldithiocarbamate, molybdenum oxysulfide dodecyldithiocarbamate, molybdenum oxysulfide 2-methyldodecyldithiocarbamate, molybdenum oxysulfide hexadecyldithiocarbamate, molybdenum oxysulfide octadecyldithiocarbamate, and molybdenum oxysulfide 2-methyloctadecyldithiocarbamate; and compounds containing their corresponding alkyl groups. Further, examples of the molybdenum oxysulfide organophosphorothioate represented by the formula [II] include molybdenum oxysulfide propylphosphorodithioate, molybdenum oxysulfide butylphosphorodithioate, molybdenum oxysulfide butenylphosphorodithioate, molybdenum oxysulfide pentylphosphorodithioate, molybdenum oxysulfide hexylphosphorodithioate, molybdenum oxysulfide heptylphosphorodithioate, molybdenum oxysulfide octylphosphorodithioate, molybdenum oxysulfide 2-ethylhexylphosphorodithioate, molybdenum oxysulfide decylphosphorodithioate, molybdenum oxysulfide dodecylphosphorodithioate, molybdenum oxysulfide octadecylphosphorodithioate, molybdenum oxysulfide oleylphosphorodithioate; and compounds containing their corresponding branched alkyl groups or alkenyl groups.

These compounds can be used either singly or in combination.

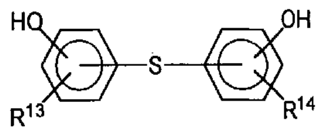
The above-described organomolybdenum compound is added to the base oil in a proportion of from 100 to 2,000 ppm, preferably from 200 to 1,500 ppm in terms of molybdenum (Mo) content on the basis of the whole weight of the lubricating oil composition. A proportion smaller than 100 ppm cannot provide sufficient friction-reducing properties, whereas a proportion greater than 2,000 ppm cannot bring about friction-reducing effects in proportion to the proportion and moreover, induces corrosion.

The organomonosulfide for use in the lubricating oil composition according to the present invention contains in its molecule a bond in which one sulfur atom exists by itself without being adjacent to any other sulfur atom, and organic compounds represented by the following formulas [III] to [VI] can be used.

$$R^9—S—R^{10} \qquad [III]$$

$$OHC—R^{11}—S—R^{12}—CHO \qquad [IV]$$

$$R^9OOC—R^{11}—S—R^{12}—COOR^{10} \qquad [V]$$



[VI]

In the above formulas [III] to [VI], R^9 and R^{10} are linear or cyclic hydrocarbon groups, and may be the same or different from each other. Examples include linear or branched alkyl groups having 1-20 carbon atoms; linear or branched alkenyl groups having 2-10 carbon atoms; and aryl groups having 6-20 aryl groups. Preferred hydrocarbon groups are alkyl groups and aryl groups, specifically linear alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, and eicosyl groups; and their corresponding branched alkyl groups. Alkyl groups are however not limited these exemplified ones, and as one of the two hydrocarbon groups, an alkyl group of a still longer chain can be used provided that the average carbon number of the two hydrocarbon groups falls within a range of from 1 to 20. On the other hand, illustrative of the aryl groups are phenyl, tolyl, xylyl, biphenyl and naphthyl groups. These aryl groups may contain one or more alkyl groups having 1-14 carbon atoms and bonded thereto. Specific usable examples of the esterified alkyl groups include methyl oleate group, methyl stearate group, oleic acid triglyceride group, methyl ester groups of vegetable oils, glycerin ester groups of vegetable oils, glycerin ester groups of animal oils, and methyl ester groups of animal oils.

R^{11} and R^{12} are linear or cyclic hydrocarbon groups, which may be the same or different from each other and have two bonding sites. Especially, alkylene groups having 1-18 carbon atoms are preferred. R^{13} and R^{14} are linear hydrocarbon groups, which are preferably alkyl groups similar to those described above for R^9 and R^{10}.

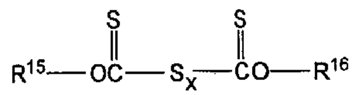
Accordingly, preferred specific examples of the organomonosulfide compound include dialkyl monosulfides, e.g., dimethyl monosulfide, diethyl monosulfide, di-n-propyl monosulfide, di-n-butyl monosulfide, di-n-pentyl monosulfide, di-n-hexyl monosulfide, di-n-cetyl monosulfide, di-n-octyl monosulfide, di-n-nonyl monosulfide, di-n-decyl monosulfide, di-n-tridecyl monosulfide, di-n-hexadecyl monosulfide, and di-n-octadecyl monosulfide; and moreover, diaryl monosulfides, e.g., diphenyl monosulfide, dibenzyl monosulfide, methyl dioleate monosulfide, methyl distearate monosulfide, and di (trioleic acid glyceride) monosulfide; as well as monosulfides containing their corresponding branched alkyl groups.

The proportion of the organomonosulfide compound ranges from 80 to 1,800, preferably from 100 ppm to 1,500 ppm in terms of sulfur (S) content. A proportion of the organomonosulfide compound smaller than 80 ppm cannot bring about sufficient effects in lowering a coefficient of friction in a low sliding speed range under reciprocating friction. On the other hand, a proportion greater than 2,000 ppm cannot bring about additional friction-reducing effects corresponding to the increase and moreover, promotes corrosion, thereby developing a practical problem.

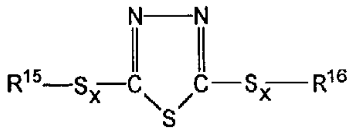
The organopolysulfide compound for use in the lubricating oil composition according to the present invention is an organic compound having a bond in which two or more sulfur atoms exist adjacent to each other in a molecule, and is represented by any one of the following formulas [VII] to [XII]:

$$R^{15}—S_x—R^{16} \qquad [VII]$$

$$R^{15}OOC—R^{17}—S_x—R^{18}—COOR^{16} \qquad [VIII]$$



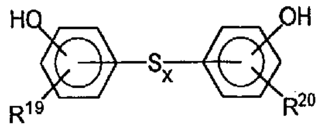
[IX]



[X]

$$OHC—R^{17}—S_x—R^{18}—CHO$$

[XI]



[XII]

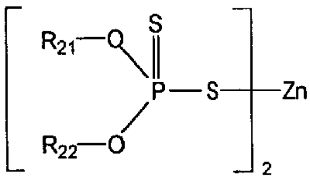
In the above formulas [VII] to [XII], R^{15} and R^{16} are linear or cyclic hydrocarbon groups, and may be the same or different from each other. Examples can be aliphatic hydrocarbon groups having 1-20 carbon atoms and aromatic hydrocarbon groups having 6-20 carbon atoms. Particularly preferred are alkyl groups, alkenyl groups, aryl groups, esterified alkyl groups and the like. Specific examples of such alkyl groups include linear alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl groups; and their corresponding branched alkyl groups. Alkyl groups are, however, not limited these exemplified ones, and alkyl groups of still longer chains can be used. On the other hand, illustrative of the aryl groups are phenyl, tolyl, xylyl, biphenyl and naphthyl groups. These aryl groups may contain one or more alkyl groups having 1-14 carbon atoms bonded thereto. Specific usable examples of the esterified alkyl groups include methyl oleate group, methyl stearate group, oleic acid triglyceride group, methyl ester groups of vegetable oils, glycerin ester groups of vegetable oils, glycerin ester groups of animal oils, and methyl ester groups of animal oils. R^{17} and R^{18} are linear or cyclic hydrocarbon groups, which may be the same or different from each other and contain two bonding sites. Particularly preferred are alkylene groups having 1-18 carbon atoms. R^{19} and R^{20} are linear hydrocarbon groups, preferably alkyl groups similar to those exemplified above. In the formulas [VII] to [XII], x is an integer of at least 2, preferably of from about 2 to 6.

Therefore, preferred specific examples of the organopolysulfide include dialkyl disulfides, dialkyl trisulfides and other dialkyl polysulfides; diphenyl disulfide, diphenyl trisulfide and other diphenyl polysulfides; dibenzyl disulfide; polyolefin polysulfides; bisalkyl polysulfanylthiadiazoles; sulfurized olefins; sulfurized fish oil; sulfurized whale oil; and sulfurized pinene. Particularly preferred are dialkyl disulfides, diphenyl disulfide, and bisalkyl polysulfanylthiadiazoles. Examples of such dialkyl disulfides include dimethyl disulfide, diethyl disulfide, di-n-propyl disulfide, di-n-butyl disulfide, di-n-pentyl-disulfide, di-n-hexyl disulfide, di-n-cetyl disulfide, di-n-octyl disulfide, di-n-nonyl disulfide, di-n-decyl disulfide, di-n-tridecyl disulfide, di-n-hexadecyl disulfide,di-n-octadecyl disulfide, methyl dioleate disulfide, methyl distearate disulfide, and di (trioleic acid glyceride) disulfide; and further, diaryl disulfides, for example, diphenyl sulfide, dibenzyl disulfide; as well as disulfides having their corresponding branched alkyl groups.

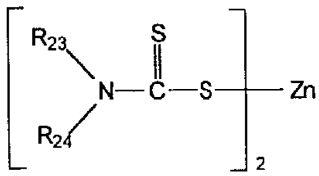
The proportion of the organopolysulfide compound ranges from 80 to 1,500 ppm, preferably from 100 to 1,200 ppm in terms of sulfur (S) content. A proportion smaller than 80 ppm cannot bring about sufficient effects for the reduction of friction, while a proportion greater than 1,500 ppm has a potential problem that corrosion wear may be promoted.

Further, the total content of sulfur derived from the organomonosulfide compound and the organopolysulfide compound ranges from 160 to 3,500 ppm, with 200 to 2,500 ppm being preferred.

For the lubricating oil composition according to the present invention, zinc dithiophosphates (ZnDTPs) and zinc dithiocarbamates (ZnDTCs) represented by the following formula [XIII] and [XIV], respectively, can optionally be used as antiwear agents.



[XIII]



[XIV]

In the above formulas [XIII] and [XIV], R^{21} to R^{24} are hydrogen atoms or hydrocarbon groups having 1-26 carbon atoms. Illustrative of the hydrocarbon groups are primary or secondary alkyl groups having 1-26 carbon atoms; alkenyl groups having 2-26 carbon atoms; cycloalkyl groups having 6-26 carbon atoms; aryl groups, alkylaryl groups and arylalkyl groups having 6-26 carbon atoms; and hydrocarbon groups containing an ester group, an ether group, one or more alcohol groups or one or more carboxyl groups. R^{21} to R^{24} are preferably alkyl groups having 2-12 carbon atoms, cycloalkyl groups having 8-18 carbon atoms or alkylaryl groups having 8-18 carbon atoms, and may be the same or different from each other.

These ZnDTPs and ZnDTCs can be used either singly or in combination. Such an antiwear agent can be used in a proportion of from 0.1 to 7 wt%, preferably from 1 wt% to 5 wt% based on the whole weight of the lubricating oil composition.

To the lubricating oil composition according to the present invention, it is possible to add various additives commonly used to date in lubricating oils, for example, other friction modifiers, metallic detergents, other antiwear agents, ashless dispersants, oxidation inhibitors, viscosity index improvers, pourpoint depressants, foam inhibitors, rust preventives, corrosion inhibitors and the like as needed to extents not impairing the object of the present invention.

Illustrative examples of the other friction modifiers include partial esters of polyhydric alcohols, amines, amides and sulfurized esters.

Illustrative examples of the metallic detergents include calcium sulfonate, calcium phenate, calcium salicylate, magnesium sulfonate, magnesium phenate and magnesium salicylate. They can be used normally in a proportion of from 0.05 to 5 wt%.

Illustrative examples of the other antiwear agents include phosphate esters and phosphite esters. They can be used normally in a proportion of from 0.05 wt% to 5 wt%.

Illustrative examples of the ashless dispersants include those of the succinimide type, succinamide type, benzylamine type and ester type. They may be used in the form of boron derivatives. They can be used normally in a proportion of form 0.5 wt% to 7 wt%.

Illustrative examples of the oxidation inhibitors include amine-type oxidation inhibitors such as alkylated diphenylamines, phenyl-α-naphthylamine and alkylated α-naphthylamines; and phenolic oxidation inhibitors such as 2,6-di-t-butyl-4-methylphenol and 4,4'-methylenebis(2,6-di-t-butylphenol). They can be used normally in a proportion of from 0.05 wt% to 4 wt%.

Illustrative examples of the viscosity index improvers include those of the polymethacrylate-type, polyisobutylene type, ethylene-propylene copolymer type, and hydrogenated styrene-butadiene copolymer type. They can be used normally in a proportion of from 0.5 wt% to 35 wt%.

Illustrative examples of the pour-point depressants include polyalkyl methacryaltes, chlorinated paraffin-naphthalene condensation products, and alkylated polystyrenes.

Illustrative examples of the foam inhibitors include dimethylpoly-siloxane and polyacrylic acid.

Illustrative examples of rust preventives include fatty acids, alkenyl succinate partial esters, fatty acid soaps, alkylsulfonic acids, fatty acid-polyhydric alcohol esters, fatty acid amines, paraffin oxide and alkylpolyoxy-ethylene ethers.

Illustrative examples of corrosion inhibitors include benzotriazole and benzimidazole.

EMBODIMENTS OF THE INVENTION

A mineral oil (kinematic viscosity: 3 mm^2/s to 20 mm^2/s at 100°C) is used as a lubricating base oil, to which molybdenum oxysulfide N,N-di(2-ethylhexyl) dithiocarbamate is added in a proportion of from 300 to 1,500 ppm in terms of molybdenum (Mo) content, diphenyl monosulfide in a proportion of from 300 to 1,800 ppm in terms of sulfur (S) content, and diphenyl disulfide in a proportion of from 400 to 1,000 ppm in terms of sulfur (S) content. Further, an antiwear agent, a metallic detergent, an ashless dispersant, an oxidation inhibitor, a viscosity index improver and/or a pour-point depressant are added in effective proportions, whereby a formulated lubricating oil composition is provided.

EXAMPLES

The present invention will hereinafter be described in further detail by the following Examples and Comparative Examples.

150 neutral oil (5.3 mm^2/s at 100°C) was used as a lubricating base oil, and the following compounds were used as additives:

1. Organomolybdenum compounds

   C_8MoDTC: Molybdenum oxysulfide N,N-di(2'-ethylhexyl) dithiocarbamate

   C_8MoDTP: Molybdenum oxysulfide di(2-ethylhexyl) phosphorodithioate

2. Organomonosulfide compounds

   C_8MS: Di-n-octyl monosulfide

DPMS: Diphenyl monosulfide

3. Organopolysulfide compounds

C_8DS: Di-n-octyl disulfide

DPDS: Diphenyl disulfide

Lubricating oil compositions were prepared by mixing additives in proportions, which are shown in Table 1 and Table 2, in the above-described base oil. With respect to the lubricating oil compositions so obtained, friction characteristics of fresh oils and used oils after NOx oxidation tests were evaluated by the following testing method.

1. Evaluation method of friction characteristics

Coefficients of friction of each of the fresh oils and used oils were measured under the following testing conditions by a reciprocating friction tester shown in Figure 1 to determine its friction characteristics under diverse friction conditions. As each coefficient of friction, a value obtained after a testing time of 20 minutes was used.

The friction test was conducted as shown in Figure 1, namely, by forming an oil film of a sample oil on a disk, placing a cylinder on the oil film and then horizontally oscillating the cylinder over a predetermined width under a predetermined load. DIN100CR_6 (HRc62, equivalent to JIS SUJ2) was used as a material for both the cylinder and the disk.

TEST CONDITIONS

	Conditions 1	Conditions 2
Load, N	400	400
Oil temperature, °C	80	80
Oscillation frequency, Hz	50	50
Amplitude, mm	0.5	2.0
(Average sliding speed, m/s)	(0.025)	(0.1)
Time, minute	20	20

Further, the used oils were obtained after conducting NOx oxidation tests under the following conditions. Similarly to the fresh oils, they were also subjected to the above-described friction tests to evaluate their friction characteristics.

NOx OXIDATION TEST CONDITIONS

Oil temperature, °C	150
Treatment time, hour	5
Nitrogen oxide gas, NO_2 concentration vol%	1
Gas flow rate, ℓ/hour	3

EXAMPLES 1-10

Examples 1-10 are directed to lubricating oil compositions of high friction-reducing properties according to the present invention as shown in Table 1.

Examples 1-3 show lubricating oil compositions of high friction-reducing properties, each of which was obtained by choosing 150 neutral oil as a base oil, employing C_8MoDTC [molybdenum oxysulfide N,N-di(2-ethylhexyl) dithiocarbamate] as an organomolybdenum compound, and using the organomonosulfide compound and the organopolysulfide compound in combination.

Examples 4-6 present lubricating oil compositions of high friction-reducing properties, each of which was obtained by employing, as an organomolybdenum compound, C_8MoDTP [molybdenum oxysulfide di(2-ethylhexyl) phosphorothioate] instead of the C_8MoDTC in Examples 1-3 and using the organomonosulfide compound and the organopolysulfide compound in combination.

Further, Examples 7-10 show lubricating oil compositions of high friction-reducing properties, each of which was obtained by employing as an organomolybdenum compound both C_8MoDTC and C_8MoDTP in combination and using the organomonosulfide compound and the organopolysulfide compound in combination.

COMPARATIVE EXAMPLES 1-9

Comparative Examples 1-6 are directed to lubricating oil compositions, each of which used the organomolybdenum compound alone or the organomolybdenum compound and the organomonosulfide compound and/or organopolysulfide but the proportion(s) was (were) outside the corresponding range(s) of the present invention, as shown in Table 2. Comparative Example 1 is directed to a lubricating oil composition which used only C_8MoDTC as an organomolybdenum compound and used neither an organomonosulfide compound nor an organopolysulfide compound. Compared with the lubricating oil composition of Example 1, the lubricating oil composition of Comparative Example 1 was additized with C_8MoDTC in the same proportion but was not additized with the above-described sulfur compound. It is therefore indicated that the fresh oil and the used oil both had high coefficients of friction and the coefficient of friction obtained under the conditions 1 was particularly high. Comparative Example 2 is directed to a lubricating oil composition, which employed C_8MS as an organomonosulfide compound and C_8DS as an organopolysulfide compound but the proportion of C_8MS was 50 ppm and was hence outside the proportion range of the organomonosulfide compound employed in the present invention. Although the organomonosulfide compound and the organopolysulfide compound were used in combination, Comparative Example 2 indicates that the coefficient of frication under the conditions 1 becomes high if the proportion of an organomonosulfide compound is less than the specific level. On the other hand, it is observed from Comparative Example 3 that the coefficient of friction under the conditions 2 becomes high if the proportion of an organopolysulfide compound is less than the specific level. Comparative Example 4 is directed to a lubricating oil composition, which employed C_8MoDTP instead of C_8MoDTC but the proportion of DPDS was 40 ppm and was hence less than the specific level. The coefficient of friction under the conditions 2 is extremely high. Comparative Examples 5-6 are directed to lubricating oil compositions, in each of which the proportion of the organomolybdenum compound was less than the specific level. Both the fresh oils and the used oils showed extremely high coefficients of friction.

Comparative Example 7 is directed to lubricating oil compositions, in each of which C_8MoDTC was added as an organomolybdenum compound in the same proportion as in Example 1 but only the organomonosulfide compound (C_8MS) was used and no organopolysulfide compound was used in combination.

Comparative Example 8 is directed to a lubricating oil composition, in which only the organopolysulfide compound (C_8DS) was used and no organomonosulfide was used in combination. The fresh oil and the used oil both had high coefficients of friction. It is therefore understood that the combined use of an organomonosulfide compound and an organopolysulfide compound is indispensable for obtaining friction-reducing effects.

According to Comparative Example 9, on the other hand, a lubricating oil composition is shown which contained both the organomonosulfide compound (C_8MS) and the organopolysulfide compound (C_8DS) but did not use any organomolybdenum compound. It is evident that sufficient friction-reducing effects cannot be obtained unless an organomolybdenum compound is used.

Thus it is seen that this invention provides a lubricating oil composition which has been obtained by adding, as essential components, an organomolybdenum compound, an organomonosulfide compound and an organopolysulfide compound in specific proportions, respectively. The lubricating oil composition has excellent friction-reducing properties under diverse sliding conditions of different sliding speeds and even in the presence of nitrogen oxide gas, can exhibit oxygen resistance to retain friction-reducing properties. The lubricating oil composition according to this invention is therefore suited as a lubricating oil for internal combustion engines, automatic transmissions, shock absorbers and power steering systems, especially for internal combustion engines.

TABLE 1

Formulation		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
C_8MoDTC, Mo:ppm		300	500	1500	-	-	-	500	200	700	400
C_8MoTP, Mo:ppm		-	-	-	200	700	1800	500	1200	1000	1500
C_8MS, S:ppm		100	500	-	1200	-	1500	300	-	-	500
C_8DS, S:ppm		300	-	300	-	-	900	1000	-	900	-
DPMS, S:ppm		-	-	1800	-	300	-	-	1500	700	-
DPDS, S:ppm		-	1000	-	500	700	-	-	400	-	1000
Base oil (150 neutral oil)		Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Coefficient of friction of fresh oil	Conditions 1	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.04
	Conditions 2	0.05	0.04	0.04	0.05	0.05	0.04	0.04	0.04	0.04	0.04
Coefficient of friction of used oil (after NO_x text)	Conditions 1	0.07	0.05	0.06	0.07	0.07	0.07	0.07	0.07	0.07	0.07
	Conditions 2	0.06	0.07	0.05	0.06	0.07	0.06	0.06	0.06	0.06	0.06

Conditions 1: oil temperature, 80°C; load, 400 N; oscillation frequency, 50 Hz; amplitude, 0.5 mm.
Conditions 2: oil temperature, 80°C; load, 400 N; oscillation frequency, 50 Hz; amplitude, 2.0 mm.
NO_x test: 150°C x 5 hours; NO_2 gas, 1 vol% in air; 3 liters/hour.

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TABLE 2

Formulation		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9
C_8MoDTC, Mo:ppm		300	500	1000	-	50	-	300	300	-
C_8MoTP, Mo:ppm		-	-	-	500	-	70	-	-	-
C_8MS, S:ppm		-	50	-	1000	-	-	100	-	100
C_8DS, S:ppm		-	300	70	-	300	-	-	300	300
DPMS, S:ppm		-	-	1500	-	1800	1000	-	-	-
DPDS, S:ppm		-	-	-	40	700	1000	-	-	-
Base oil (150 neutral oil)		Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Coefficient of friction of fresh oil	Conditions 1	0.12	0.1	0.08	0.06	0.13	0.12	0.10	0.11	0.14
	Conditions 2	0.07	0.07	0.11	0.1	0.14	0.14	0.13	0.08	0.15
Coefficient of friction of used oil (after NO_x text)	Conditions 1	0.13	0.12	0.09	0.07	0.15	0.14	0.12	0.13	0.15
	Conditions 2	0.11	0.09	0.13	0.14	0.15	0.15	0.16	0.11	0.16

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A lubricating oil composition comprising: a lubricating base oil, and an organomolybdenum compound in a proportion of from 100 to 2,000 ppm in terms of molybdenum (Mo) content, an organomonosulfide compound in a proportion of from 80 to 2,000 ppm in terms of sulfur (S) content, and an organopolysulfide compound in a proportion of from 80 to 1,500 ppm in terms of sulfur (S) content.

2. The lubricating oil composition of claim 1 wherein the lubricating oil has a viscosity in the range of 3 mm^2/s to 20 mm^2/s at 100°C, contains 3 wt% or less aromatic components (% C_A) has a sulfur content of 50 ppm or less and a nitrogen content of 50 ppm or less, the organomolybdenum compound is present in a proportion of from 200 to 1,500 ppm in terms of molybdenum, the organic monosulfide is present in a proportion of from 100 to 1,500 ppm in terms of sulfur content and the organopolysulfide compound is present in a proportion of from 100 to 1,200 ppm in terms of sulfur content.

3. A method for enhancing the friction reducing and friction reduction retention properties of a lubricating oil comprising adding to the lubricating oil an organomolybdenum compound in a proportion of from 100 to 2,000 ppm in terms of molybdenum content, an organomonosulfide compound in a proportion of from 80 to 2,000 ppm in terms of sulfur content and an organopolysulfide compound in a proportion of from 80 to 1,500 ppm in terms of sulfur content.

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