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(54) Title: LUBRICATING OIL COMPOSITION

(57) Abstract: The present invention provides a lubricating composition comprising a base oil, an aspartic acid derivative, a succinic acid derivative and a thiophosphate ester. In a further aspect the present invention provides the use of the lubricating composition for improving one or more of rust-prevention and extreme-pressure properties.

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LUBRICATING OIL COMPOSITION

This invention relates to lubricating compositions and among them to the generality of industrial lubricating oils using refined base oils, and in particular relates to lubricating compositions used as machine oils, hydraulic oils, turbine oils, compressor oils, gear oils, sliding friction oils, bearing oils and calibration oils.

Corrosion resistance is required as a fundamental property of lubricating oils in machinery installations so as to maintain performance. This is because the lubricating oil temperature within tanks in mechanical apparatus rises and falls in accordance with conditions of use, and so therefore the lubricating oil within the tanks may be subject to admixture with condensed water, or to admixture with moisture because of leaks from cooling water pipes.

Also, in recent years, because mechanical apparatus has become faster, more load bearing and more efficient, the risks of seizures on friction surfaces due to breakdown of the lubricating oil film have increased. Extreme-pressure agents, which maintain extreme-pressure properties by reacting with metallic surfaces on friction planes, are added to lubricating oils used under such harsh conditions, with a view to preventing adhesion between friction surfaces. However, it is known that rust preventatives impair the effect of extreme-pressure agents on metallic surfaces.

It is also known that in order to obtain the rust-preventing effect as mentioned above an N-acyl-N-hydrocarbon oxyalkyl aspartic acid ester can be blended

in the lubricating oil composition (see Japanese Laid-open Patent H6-200268 (1994)), and that β-dithiophosphoryl propionic acid can be used as an extreme-pressure agent (see Japanese Laid-open Patent 2002-294268).

This invention is intended to obtain an industrial lubricating oil which not only has excellent rust-preventing properties but also has excellent extreme-pressure properties.

This invention pertains to a lubricating oil composition in which an aspartic acid derivative, a succinic acid derivative and a thiophosphate ester are incorporated as additives in a base oil which preferably is a mineral oil or a synthetic oil.

If both an aspartic acid derivative and a succinic acid derivative are used as additives in a base oil, excellent rust-preventing properties are obtained, and the excellent rust-preventing performance is obtained even though the amounts added are substantially reduced. When the aspartic acid derivative and succinic acid derivative are used together, it is also possible, by reducing the amounts thereof, even more effectively to exhibit the extreme-pressure performance of the thiophosphate ester used as an extreme-pressure agent, and a lubricating oil composition with excellent rust prevention and excellent extreme-pressure properties can be obtained.

Also, by further adding at least one compound selected from amine compounds, amide compounds, and ester compounds, a lubricating composition with even more excellent anti-rust and extreme pressure properties is obtained.

According to this invention, it is possible to obtain a superior lubricating oil composition in which the generation of rust is effectively inhibited and which has excellent extreme-pressure properties. Accordingly, it is possible to offer a lubricating oil composition which responds to the faster speeds, higher pressures, greater compactness and improved endurance of industrial machines, and which has excellent extreme-pressure properties while maintaining good rust prevention.

Also by means of this invention, it is possible to reduce substantially the amount of rust preventative added while at the same time offering economically a lubricating oil composition which has superior extreme-pressure performance. Such a lubricating oil composition can be widely used for the generality of industrial lubricating oils, and among these it can be used effectively for lubricating oils using refined base oils, in particular as machine oils, hydraulic oils, turbine oils, compressor oils, gear oils, sliding friction oils, bearing oils and calibration oils.

For the base oil of the present lubricating oil composition it is possible to use mineral oils describable as highly refined base oils, and synthetic oils, and in particular it is possible to use, singly or as mixtures, base oils which belong to Group I, Group II, Group III, Group IV and so on of the API (American Petroleum Institute) base oil categories. The base oils used here typically have an elemental sulphur content of less than 700 ppm and preferably less than 500 ppm. The density will typically be from 0.8 to 0.9. The aromatic content will typically be not more than 5% and preferably not more than 3%.

Group I base oils include, for example, paraffinic mineral oils obtained by appropriate use of a suitable combination of refining processes such as solvent refining, hydrorefining, and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil. The viscosity index (ASTM D2270) is typically from 80 to 120 and preferably from 95 to 110. The kinematic viscosity at 40°C (ASTM D445) is typically from 2 to 680 mm^2/s and preferably from 8 to 220 mm^2/s. Also, the total sulphur content is typically less than 700 ppm and preferably less than 500 ppm. The total nitrogen content is typically less than 50 ppm and preferably less than 25 ppm. In addition, oils with an aniline point of from 80 to 150°C and preferably from 90 to 120°C are preferred.

Group II base oils include, for example, paraffinic mineral oils obtained by appropriate use of a suitable combination of refining processes such as hydrorefining and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil. Group II base oils refined by hydrorefining methods such as the Gulf Company method have a total sulphur content of less than 10 ppm and an aromatic content of not more than 5% and so are suitable for this invention. The viscosity of these base oils is not specially limited, but the viscosity index (ASTM D2270) is typically 80 to 120 and preferably 100 to 120. The kinematic viscosity at 40°C (ASTM D445) is typically 2 to 680 mm^2/s and preferably 8 to 220 mm^2/s. Also, the total sulphur content is typically less than 300 ppm, preferably less than 200 ppm and even more preferably less than 10 ppm. The total nitrogen content is typically less than 10 ppm and preferably less than 1 ppm. In addition, oils with an

aniline point of 80 to 150°C and preferably 100 to 135°C are preferred.

Suitable Group III base oils and Group II+ base oils include paraffinic mineral oils manufactured by a high degree of hydrorefining in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil, base oils refined by the Isodewax process which dewaxes and substitutes the wax produced by the dewaxing process with isoparaffins, and base oils refined by the Mobil wax isomerisation process. They include those that may be designated as "synthetic oils" according to the rulings of the NAD (National Advertising Division) which is responsible for advertising adjudications in America. The viscosity of these base oils is not specially limited, but the viscosity index (ASTM D2270) is typically 95 to 145 and preferably 100 to 140. The kinematic viscosity at 40°C (ASTM D445) is typically 2 to 680 mm^2/s and even more preferably 8 to 220 mm^2/s. Also, the total sulphur content is typically 0 to 100 ppm and preferably less than 10 ppm. The total nitrogen content is typically less than 10 ppm and preferably less than 1 ppm. In addition, oils with an aniline point of 80 to 150°C and preferably 110 to 135°Care preferred.

GTLs (gas to liquid; or "GTL-derived base oils") synthesised by the Fischer-Tropsch method of converting natural gas to liquid fuel have a very low sulphur content and aromatic content compared with mineral oil base oils refined from crude oil and have a very high paraffin constituent ratio, and so have excellent oxidative stability, and because they also have extremely small evaporation losses, they are suitable as base oils for this invention. The viscosity of GTL base oils is not specially limited, but normally the viscosity index (ASTM

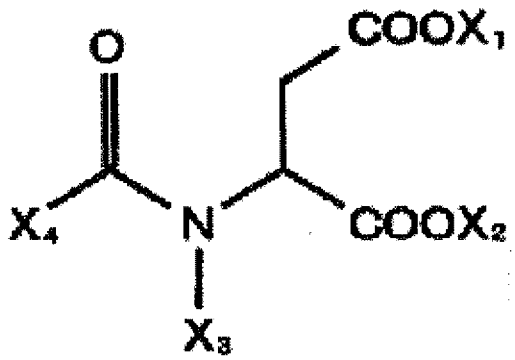
D2270) is typically 130 to 180 and preferably 140 to 175. Also, the kinematic viscosity at 40°C (ASTM D445) is typically 2 to 680 mm^2/s and preferably 5 to 120 mm^2/s. Normally the total sulphur content is also less than 10 ppm and the total nitrogen content less than 1 ppm. A commercial example of such a GTL base oil is Shell XHVI (registered trademark).

As examples of synthetic oils mention may be made of polyolefins, alkylbenzenes, alkylnaphthalenes, esters, polyoxyalkylene glycols, polyphenyl ethers, dialkyldiphenyl ethers, fluorine-containing compounds (perfluoropolyethers, fluorinated polyolefins) and silicone oils.

The aforementioned polyolefins include polymers of various olefins or hydrides thereof. Any olefin may be used, and as examples mention may be made of ethylene, propylene, butene and α-olefins with five or more carbons. In the manufacture of polyolefins, one kind of the aforementioned olefins may be used singly or two or more kinds may be used in combination. Particularly suitable are the polyolefins called poly-α-olefins (PAO). These are base oils of Group IV. The viscosity of these synthetic oils is not specially limited, but the kinematic viscosity at 40°C (ASTM D2270) is preferably from 2 to 680 mm^2/s and more preferably 8 to 220 mm^2/s.

The amount of the aforementioned base oil to be incorporated in the lubricating oil composition of this invention is not specially limited, but, taking as a basis the total amount of the lubricating oil composition, is typically at least 60% by mass, preferably at least 80% by mass, more preferably at least 90% by mass, and yet more preferably at least 95% by mass.

The aspartic acid derivatives are shown by the undermentioned General Formula 1.



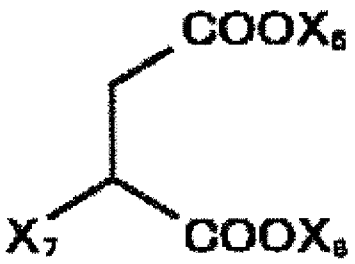
(Formula 1)

In the aforementioned General Formula 1, X1 and X2 are each hydrogen or alkyl groups, alkenyl groups or hydroxyalkyl groups with 3 to 6 carbons which may be the same or different, and preferably respectively a 2-methylpropyl group and a tertiary butyl group. X3 has 1 to 30 carbons and is an alkyl group or an alkenyl group, or an alkyl group having ether bonds, or a hydroxyalkyl group. For example, an octadecyl group, an alkoxypropyl group, a 3-(C6-C18)hydrocarbonoxy(C3-C6) alkyl group, and more preferably a cyclohexyloxypropyl group, a 3-octyloxypropyl group, a 3-isooctyloxypropyl group, a 3-decyloxypropyl group, a 3-isodecyloxypropyl group and a 3-(C12-C16)alkoxypropyl group are suitable. X4 is a saturated or unsaturated carboxylic acid group comprising 1 to 30 carbons, or an alkyl group, alkenyl group group or hydroxyalkyl group comprising 1 to 30 carbons. For example, a propionic acid group or a propionyl acid group is suitable.

The aforementioned aspartic acid derivatives typically have an acid number as determined by JIS K2501 of from 10 to 200 mgKOH/g and preferably from 50 to 150 mgKOH/g. The amount of aspartic acid derivatives used in the lubricating oil composition is approximately from 0.001 to 0.5% by mass, preferably approximately from

0.001 to 0.1% by mass and more preferably approximately from 0.005 to 0.05% by mass. One kind or a mixture of these aspartic acid derivatives may be used.

The succinic acid derivatives are shown by the undermentioned General Formula 2.



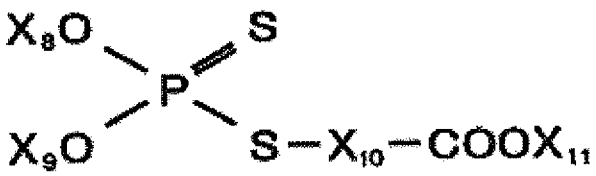
(Formula 2)

In the aforementioned General Formula 2, X5 and X6 are each hydrogen or alkyl groups, alkenyl groups or hydroxyalkyl groups with 3 to 6 carbons which may be the same or different, and preferably are hydrogen atoms, 1-hydroxypropyl groups, 2-hydroxypropyl groups, 2-methylpropyl groups or tertiary butyl groups. X7 has 1 to 30 carbons and is an alkyl group or an alkenyl group, or an alkyl group having ether bonds, or a hydroxyalkyl group. For example, a methyl group, an ethyl group, a propyl group, a butyl group, pentyl group, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a dodecylene group, a tridecyl group, a tetradecyl group, a tetradecylene group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, an octadecylene group, an eicosyl group, a docosyl group, an alkoxypropyl group, a 3-(C6-C18)hydrocarbonoxy(C3-C6) alkyl group, and more preferably a tetraisopropyl group, an oleyl group, a cyclohexyloxypropyl group, a 3-octyloxypropyl group, a 3-isooctyloxypropyl group, a 3-decyloxypropyl group, a 3-isodecyloxypropyl group and a

3-(C12-C16)alkoxypropyl group are suitable. Aminated forms of these compounds are also suitable.

The aforementioned succinic acid derivatives typically have an acid number as determined by JIS K2501 of from 10 to 300 mgKOH/g and preferably from 30 to 200 mgKOH/g. The amount of succinic acid derivatives used in the lubricating oil composition is approximately from 0.001 to 0.5% by mass, preferably approximately from 0.001 to 0.1% by mass and more preferably approximately from 0.005 to 0.05% by mass. One kind or a mixture of these succinic acid derivatives may be used.

Thiophosphate ester compounds can be incorporated in this invention. As examples of the thiophosphate compounds, mention may be made of the thiophosphate esters shown in the undermentioned General Formula (3) and General Formula (4).

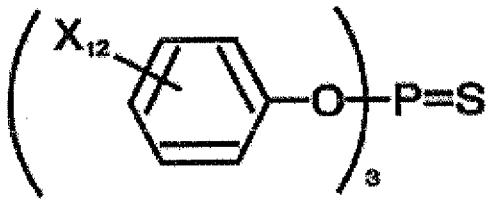


(Formula 3)

In the aforementioned General Formula (3), X8 and X9 may be the same or different. Each denotes a hydrogen atom or a hydrocarbon group of 1 to 30 carbons, and mention may be made of alkyl groups, alkenyl groups, aryl groups, alkylaryl groups and arylalkyl groups. X10 denotes an alkylene group of 1 to 20 carbons, and X11 denotes a hydrogen atom or a hydrocarbon group of 1 to 30 carbons. Among the aforementioned phosphorylated carboxylic acids, mention may be made of β-diothiophosphoryl carboxylic acid derivatives.

As a specific example of these β-diothiophosphoryl carboxylic acids where this X11 is a hydrogen atom, mention may be made of 3-(di-isobutoxy-thiophosphorylsulphanyl)-2-methyl-propionic acid, and as

an example of a β-diothiophosphoryl carboxylic acid ester where X11 is an ethyl group, mention may be made of ethyl-3-[[bis(1-methylethoxy)phosphinothioyl]thio]propionate.



(Formula 4)

In the aforementioned General Formula (4), X12 denotes a hydrogen atom or a hydrocarbon group with 1 to 30 carbons. Mention may be made specifically of triphenyl phosphorothionate or nonylphenyl phosphorothionate.

The amount of thiophosphate ester compounds in the lubricating composition of this invention is not specially limited, but is preferably of the order of approximately 0.001 to 1% by mass in the composition, and more preferably of the order of approximately 0.002 to 0.5% by mass. If the amount of thiophosphate ester compounds is less than the aforementioned lower limit, there will be a tendency for sufficient lubricating effect not to be obtained. On the other hand, even if it is added in excess of the aforementioned upper limit, there will be a tendency for the effect in improvement of lubricating properties not to match the amount added, and furthermore there is a danger that the thermal and oxidative stability, or the hydrolytic stability, will be reduced. These thiophosphate ester compounds may be used singly or in mixtures of several kinds.

Amine compounds can be blended into this lubricating oil composition. Aliphatic amine compounds can be used for these amine compounds, and as examples mention may be made of the primary amines shown by General Formula (5), the secondary amines shown by General Formula (6), the

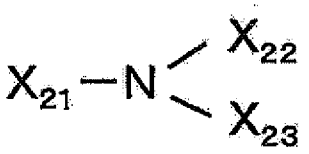
diamines shown by General Formula (7) and the tertiary amines shown by General Formula (8).

$$H_2N-X_{13}$$ (Formula 5)

In the aforementioned General Formula 5, X13 is an alkyl group or alkenyl group of 1 to 30 carbons. As examples of such compounds, mention may be made of laurylamine, coconut amine, n-tridecylamine, myristylamine, n-pentadecylamine, n-palmitylamine, n-heptadecylamine, n-stearylamine, isostearylamine, n-nonadecylamine, n-eicosylamine, n-heneicosylamine, n-docosylamine, n-tricosylamine, n-pentacosylamine, oleylamine, beef tallow amine, hydrogenated beef tallow amine and soybean amine. The number of carbons in X13 should preferably be 8 to 24, and more preferably 12 to 18. Also, X13 may be a straight-chain aliphatic, a branched-chain aliphatic or a tertiary alkyl group.

$$X_{14}-NH-X_{15}$$ (Formula 6)

In the aforementioned General Formula 6, X14 and X15 are alkyl groups or alkenyl groups of 1 to 30 carbons. As examples of such compounds, mention may be made of dilaurylamine, dicoconut amine, di-n-tridecylamine, di-n-myristylamine, di-n-pentadecylamine, di-n-palmitylamine, di-n-heptadecylamine, di-n-stearylamine, diisostearylamine, di-n-nonadecylamine, di-n-eicosylamine, di-n-heneicosylamine, di-n-docosylamine, di-n-tricosylamine, di-n-pentacosylamine, dioleylamine, di-beef tallow amine, di-hydrogenated beef tallow amine and di-soybean amine. The number of carbons in X14 and X15 should preferably be 8 to 24, and more preferably 12 to 18. X14 and X15 may be the same or different.

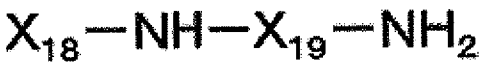


(Formula 7)

In the aforementioned General Formula 7, X21 is an alkyl group or alkenyl group of 1 to 30 carbons. The number of carbons in X21 is preferably 1 to 20. X22 or X23 is an alkyl group, an alkenyl group or a hydroxyalkyl group of 1 to 20 carbons. The number of carbons in X22 or X23 is preferably 1 to 18. Assuming X21 is a methyl group, examples of dialkylmethylamines include dioctylmethylamine, dinonylmethylamine, didecylmethylamine, diundecylmethylamine, dilaurylmethylamine, ditridecylmethylamine, dimyristylmethylamine, ditetradecylmethylamine, dipentadecylmethylamine, dipalmitylmethylamine, diheptadecylmethylamine, dioleylmethylamine, distearylmethylamine, diisostearylmethylamine, dinonadecylmethylamine, dieicosylmethylamine, di-coconut methylamine, di-beef tallow methylamine, di-hydrogenated beef tallow methylamine and di-soybean methylamine.

Assuming X22 or X23 is a methyl group, examples of alkyldimethylamines include octyldimethylamine, nonyldimethylamine, decyldimethylamine, undecyldimethylamine, lauryldimethylamine, tridecyldimethylamine, myristyldimethylamine, tetradecyldimethylamine, pentadecyldimethylamine, palmityldimethylamine, heptadecyldimethylamine, oleyldimethylamine, stearyldimethylamine, isostearyldimethylamine, nonadecyldimethylamine, eicosyldimethylamine, coconut dimethylamine, beef tallow dimethylamine, hydrogenated beef tallow dimethylamine and soybean dimethylamine.

Assuming X22 or X23 is a hydroxyalkyl group, examples of N-alkyldiethanolamines include N-octyldiethanolamine, N-nonyldiethanolamine, N-decyldiethanolamine, N-undecyldiethanolamine, N-lauryldiethanolamine, N-tridecyldiethanolamine, N-myristyldiethanolamine, N-tetradecyldiethanolamine, N-pentadecyldiethanolamine, N-palmityldiethanolamine, N-heptadecyldiethanolamine, N-oleyldiethanolamine, N-stearyldiethanolamine, N-isostearyldiethanolamine, N-nonadecyldiethanolamine, N-eicosyldiethanolamine, N-coconut diethanolamine, N-beef tallow diethanolamine, N-hydrogenated beef tallow diethanolamine and N-soybean diethanolamine, and examples of N-alkyldipropanolamines include N-octyldipropanolamine, N-nonyldipropanolamine, N-decyldipropanolamine, N-undecyldipropanolamine, N-lauryldipropanolamine, N-tridecyldipropanolamine, N-myristyldipropanolamine, N-tetradecyldipropanolamine, N-pentadecyldipropanolamine, N-palmityldipropanolamine, N-heptadecyldipropanolamine, N-oleyldipropanolamine, N-stearyldipropanolamine, N-isostearyldipropanolamine, N-nonadecyldipropanolamine, N-eicosyldipropanolamine, N-coconut dipropanolamine, N-beef tallow dipropanolamine, N-hydrogenated beef tallow dipropanolamine and N-soybean dipropanolamine.



(Formula 8)

In the aforementioned General Formula 8, X18 is an alkyl group or alkenyl group of 1 to 30 carbons. The number of carbons in X18 is preferably 8 to 24 and more preferably 12 to 18. X19 is an alkylene group of 1 to 12 carbons. The number of carbons in X19 is preferably 1 to 8 and more preferably 2 to 4.

Examples of ethylenediamines include N-octyl-1,2-ethylenediamine, N-nonyl-1,2-ethylenediamine, N-decyl-

1,2-ethylenediamine, N-undecyl-1,2-ethylenediamine, N-lauryl-1,2-ethylenediamine, N-tridecyl-1,2-ethylenediamine, N-myristyl-1,2-ethylenediamine, N-tetradecyl-1,2-ethylenediamine, N-pentadecyl-1,2-ethylenediamine, N-palmityl-1,2-ethylenediamine, N-heptadecyl-1,2-ethylenediamine, N-oleyl-1,2-ethylenediamine, N-stearyl-1,2-ethylenediamine, N-isostearyl-1,2-ethylenediamine, N-nonadecyl-1,2-ethylenediamine, N-eicosyl-1,2-ethylenediamine, N-coconut-1,2-ethylenediamine, N-beef tallow-1,2-ethylenediamine, N-hydrogenated beef tallow-1,2-ethylenediamine and N-soybean-1,2-ethylenediamine.

Examples of propylenediamines include N-octyl-1,3-propylenediamine, N-nonyl-1,3-propylenediamine, N-decyl-1,3-propylenediamine, N-undecyl-1,3-propylenediamine, N-lauryl-1,3-propylenediamine, N-tridecyl-1,3-propylenediamine, N-myristyl-1,3-propylenediamine, N-tetradecyl-1,3-propylenediamine, N-pentadecyl-1,3-propylenediamine, N-palmityl-1,3-propylenediamine, N-heptadecyl-1,3-propylenediamine, N-oleyl-1,3-propylenediamine, N-stearyl-1,3-propylenediamine, N-isostearyl-1,3-propylenediamine, N-nonadecyl-1,3-propylenediamine, N-eicosyl-1,3-propylenediamine, N-coconut-1,3-propylenediamine, N-beef tallow-1,3-propylenediamine, N-hydrogenated beef tallow-1,3-propylenediamine and N-soybean-1,3-propylenediamine.

Examples of butylenediamines include N-octyl-1,4-butylenediamine, N-nonyl-1,4-butylenediamine, N-decyl-1,4-butylenediamine, N-undecyl-1,4-butylenediamine, N-lauryl-1,4-butylenediamine, N-tridecyl-1,4-butylenediamine, N-myristyl-1,4-butylenediamine, N-tetradecyl-1,4-butylenediamine, N-pentadecyl-1,4-butylenediamine, N-palmityl-1,4-butylenediamine, N-

heptadecyl-1,4-butylenediamine, N-oleyl-1,4-butylenediamine, N-stearyl-1,4-butylenediamine, N-isostearyl-1,4-butylenediamine, N-nonadecyl-1,4-butylenediamine, N-eicosyl-1,4-butylenediamine, N-coconut-1,4-butylenediamine, N-beef tallow-1,4-butylenediamine, N-hydrogenated beef tallow-1,4-butylenediamine and N-soybean-1,4-butylenediamine.

The aforementioned amine compounds preferably have a base number as determined by JIS K2501 of 10 to 800 mgKOH/g and more preferably 100 to 500 mgKOH/g. Approximately 0.005 to 5% by mass, and preferably approximately 0.01 to 1% by mass, of at least one kind of these amine compounds selected from the aforementioned groups is preferably used in the lubricating composition, singly or in suitable combinations.

As examples of amide compounds in this invention, mention may be made of amide compounds which are products based on fatty acids and monoamines or polyamines.

$$X_{20}CONH_2$$

(Formula 9)

Assuming the amide compound is based on a fatty acid and a monoamine, in the aforementioned General Formula 9, X20 is an alkyl group or alkenyl group of 1 to 30 carbons. For example, mention may be made of laurylamide, coconut amide, n-tridecylamide, myristylamide, n-pentadecylamide, n-palmitylamide, n-heptadecylamide, n-stearylamide, isostearylamide, nononadecylamide, n-eicosylamide, n-heneicosylamide, n-docosylamide, n-tricosylamide, n-pentacosylamide, oleylamide, beef tallow amide, hydrogenated beef tallow amide and soybean amide. The number of carbons in X20 is typically 6 to 30, preferably 8 to 24 and more preferably 12 to 18. X20 may

also be a straight-chain aliphatic, a branched-chain aliphatic or a tertiary alkyl group.

Assuming the amide compound is based on a polyamine and a fatty acid, mention be made for example of polyalkylene polyamides of saturated or unsaturated fatty acids having 1 to 24 carbons and aliphatic amines, such as isostearic acid triethylene tetramide, isostearic acid tetraethylene pentamide, oleic acid diethylene triamide and oleic acid diethanol amide.

It is possible to incorporate fatty acid esters of polyhydric alcohols in the lubricating composition of this invention.

For example, it is possible to use partial or complete esters of saturated or unsaturated fatty acids having 6 to 30 carbons, preferably 8 to 24 carbons, more preferably 8 to 18 carbons, and polyols such as glycerine, sorbitan, alkylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol and xylitol.

As examples of esters of glycerin, mention may be made of glycerin monolaurate, glycerin monostearate, glycerin monopalmitate, glycerin monooleate, glycerin dilaurate, glycerin distearate, glycerin dipalmitate, glycerin dioleate.

As examples of esters of sorbitan, mention may be made of sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan dilaurate, sorbitan dipalmitate, sorbitan distearate, sorbitan dioleate, sorbitan tristearate, sorbitan dilaurate, sorbitan trioleate, sorbitan tetraoleate, sorbitan sesquioleate.

As examples of esters of alkylene glycol, mention may be made of ethylene glycol monolaurate, ethylene glycol monostearate, ethylene glycol monooleate, ethylene

glycol dilaurate, ethylene glycol distearate, ethylene glycol dioleate, propylene glycol monolaurate, propylene glycol monostearate, propylene glycol monooleate, propylene glycol dilaurate, propylene glycol distearate, propylene glycol dioleate.

As examples of esters of neopentyl glycol, mention may be made of neopentyl glycol monolaurate, neopentyl glycol monostearate, neopentyl glycol monooleate, neopentyl glycol dilaurate, neopentyl glycol distearate, neopentyl glycol dioleate.

As examples of esters of trimethylolpropane, mention may be made of trimethylolpropane monolaurate, trimethylolpropane monostearate, trimethylolpropane monooleate, trimethylolpropane dilaurate, trimethylolpropane distearate, trimethylolpropane dioleate.

As examples of esters of pentaerythritol, mention may be made of pentaerythritol monolaurate, pentaerythritol monostearate, pentaerythritol monooleate, pentaerythritol dilaurate, pentaerythritol distearate, pentaerythritol dioleate.

As examples of esters of xylitol, mention may be made of xylitol monolaurate, xylitol monostearate, xylitol monooleate, xylitol dilaurate, xylitol distearate, xylitol dioleate, xylitol trioleate.

Polyol esters such as carboxylic acid ester, preferably partial esters (reactant) of unsaturated fatty (carboxylic) acids and polyol are good.

It is possible to incorporate epoxidised ester compounds in this invention. Epoxidised ester compounds are manufactured by epoxidising esters of rapeseed oil, soybean oil, linseed oil, castor oil, coconut oil, palm oil palm kernel oil, sunflower oil, rice bran oil,

safflower oil, beef tallow, pork tallow and so on. For example, mention may be made of epoxidised rapeseed oil esters, epoxidised soybean oil esters, epoxidised linseed oil esters, epoxidised castor oil esters and epoxidised safflower oil esters, and those manufactured by epoxidising oleic acid esters such as methyl epoxystearate, butyl epoxystearate and octyl epoxystearate. Also, the alcohol residues of the esters are alkyl groups, or alkyl groups having ether bonds, or hydroxyalkyl groups, and more preferably are butyl groups, isobutyl groups and 2-ethylhexyl groups. As examples, mention may be made of epoxidised rapeseed oil fatty acid isobutyl ester, epoxidised rapeseed oil fatty acid 2-ethylhexyl ester and epoxidised linseed oil fatty acid butyl ester. The essential constituents of ordinary rapeseed oil fatty acids are fatty acids having 18 carbons with oleic acid 63%, linolic acid 20% and linolenic acid 8%. The essential constituents of linseed fatty acids are fatty acids having 18 carbons with oleic acid 21%, linolic acid 13% and linolenic acid 57%.

It is possible to incorporate mono-alcohol compounds of 6 to 30 carbons in the lubricating composition of this invention. These mono-alcohols are consisting of an alkyl group or alkenyl group of 6 to 30 carbons, linear or branched, saturated or unsaturated, preferably 8 to 24 carbons more preferably 10 to 22, moreover preferably 12 to 22 carbons.

As examples of mono-alkylalcohol, mention may be made of octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol (stearyl alcohol), nonadecanol, icosanol, henicosanol, docosanol (behenyl alcohol), tricosanol, tetracosanol.

As examples of mono-alkenyl-alcohol, mention may be made of octenol, nonenol, decenol, undecenol, dodecenol, tridecenol, tetradecenol, pentadecenol, hexadecenol, heptadecenol, octadecenol (oleyl alcohol), nonadecenol, icosenol, henicosenol, docosenol, tricosenol, tetracosenol.

Mixtures of these two or more compounds are also good. In case of less than 6 carbons or more than 30 carbons of alcohol, lubricating oil composition have poor solubility against base oil or poor heat stability in this invention.

It is possible to incorporate carboxylic acids of monocarboxylic acids (monocarboxylates), polycarboxylic acids (polycarboxylates), cyclic carboxylic acids (cyclic carboxylates), heterocyclic carboxylic acids (heterocyclic carboxylates) in the lubricating composition of this invention.

Aforementioned monocarboxylic acids typically have a carboxylic group comprising of 6 to 30 carbons preferably 8 to 24.

As examples of saturated fatty acids, mention may be made of mono-carboxylic acids with carbon number 8 to 24, linear or branched aliphatic group, octanoic acid (caprylic acid), nonanoic acid (pelargonic acid), decanoic acid (capric acid), undecanioc acid, dodecanoic acid (lauric acid), tridecanoic acid, tetradecanoic acid (myristic acid), pentadecanoic acid, hexadecanoic acid (palmitic acid), heptadecanoic acid, octadecanoic acid (stearic acid), nonadecanoic acid, icosanoic acid, henicosanoic acid, docosanoic acid, tricosanoic acid, tetracosanoic acid.

As examples of unsaturated fatty acids, mention may be made of mono-carboxylic acids with carbon number 8 to

24, preferably 12 to 22, linear or branched aliphatic group, octenoic acid, nonenoic acid, decenoic acid, undecenioc acid, dodecenoic acid, tridecenoic acid, tetradecenoic acid, pentadecenoic acid, hexadecenoic acid, heptadecenoic acid, octadecenoic acid (oleic acid), nonadecenoic acid, icosenoic acid, henicosenoic acid, docosenoic acid, tricosenoic acid, tetracosenoic acid.

As examples of other monocarboxylic acids, saturated or unsaturated, linear or branched, mention may be made of N-methyl-N-(1-oxodecyl)glycine, N-methyl-N-(1-oxoundecyl)glycine, N-methyl-N-(1-oxododecyl)glycine, N-methyl-N-(1-oxotridecyl)glycine, N-methyl-N-(1-oxotetradecyl)glycine, N-methyl-N-(1-oxopentadecyl)glycine, N-methyl-N-(1-oxohexadecyl)glycine, N-methyl-N-(1-oxoheptadecyl)glycine, N-methyl-N-(1-oxooctadecyl)glycine, N-methyl-N-(1-oxo-9-octadecenyl)glycine, N-methyl-N-(1-oxononadecyl)glycine, N-methyl-N-(1-oxoicosyl)glycine.

As examples of di-carboxylic acids, mention may be made of, saturated or unsaturated, linear or branched, 1,6-hexanedioic acid (adipic acid), 1,7-heptanedioic acid (pimelic acid), 1,8-octanedioic acid (suberic acid), 1,9-nonanedioic acid (azelaic acid), 1,10-decanedioic acid1 (sebacic acid), 1,6-hexenedioic acid, 1,7-heptenedioic acid, 1,8-octenedioic acid, 1,9-nonenedioic acid, 1,10-decenedioic acid.

As examples of tri-carboxylic acids, saturated or unsaturated, linear or branched, mention may be made of hexane-tricarboxylic acid, heptane-tricarboxylic acid, octane-tricarboxylic acid, nonane-tricarboxylic acid, decane-tricarboxylic acid.

For tetracarboxylic acids, mention may be made of saturated or unsaturated, linear or branched acids.

For cyclic carboxylic acids (cyclic carboxylates) having one or more carboxylic groups, for instance, mention may be made of cyclohexane-monocarboxylic acid, methylcyclohexane-monocarboxylic acid, ethylcyclohexane-monocarboxylic acid, propylcyclohexane-monocarboxylic acid, butylcyclohexane-monocarboxylic acid, pentylcyclohexane-monocarboxylic acid, hexylcyclohexane-monocarboxylic acid, heptylcyclohexane-monocarboxylic acid, octylcyclohexane-monocarboxylic acid, cycloheptane-monocarboxylic acid, cyclooctane-monocarboxylic acid, trimethylcyclopentane-dicarboxylic acid (camphoric acid: cis-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid), may contain 3 to 40 carbons, benzenecarboxylic acid (benzoic acid), methylbenzoic acids (toluic acid), dimethylbenzoic acids(xylic acid), ethylbenzoic acid, propylbenzoic acid, benzene-dicarboxylic acids (phthalic acid, isophthalic acid, terephthalic acid), benzene-tricarboxylic acids (hemimellitic acid, trimellitic acid, trimesic acid), benzene-tetracarboxylic, acids (mellophanic acid, prehnitic acid, pyromellitic acid), naphthalenecarboxylic acids (1- or 2-naphthoic acid), 2-phenylpropionic acid(hydroatropic acid), 3-phenylpropionic acid (hydrocinnamic acid), phenylpropenoic acid (atropic acid, cinnamic acid), 2-phenyl-2-propenoic acid (atropic acid), 3-phenyl-2-propenoic acid (cinnamic acid), methylphenoxyacetic acid, ethylphenoxyacetic acid, butylphenoxyacetic acid, hexylphenoxylacetic acid, heptylphenoxylacetic acid, octylphenoxyacetic acid, nonylphenoxyacetic acid, decylphenoxyacetic acid, alkylphenoxyacetic acids, salicylic acid, alkylsalicylic acids.

As examples of the aforementioned heterocycliccarboxylic acids, mention may be made of tributyl phosphate, for example, furancarboxylic acids, thiophenecarboxylic acids, pyridinecarboxylic acids (nicotinic acid, isonicotinic acid) etc., and those are having 5 to 40 carbons.

It is possible to add phosphorus compounds other than the aforementioned thiophosphate ester compounds to the lubricating oil composition of this invention, and by this means it is possible to impart further wear-resisting properties and extreme-pressure properties. As examples of such phosphorus compounds, mention may be made of phosphate esters, acidic phosphate esters, amine salts of acidic phosphate esters, phosphite esters, phosphorothionates, zinc dithiophosphates, phosphorus-containing carboxylic acids and phosphorus-containing carboxylic acid esters. These phosphorus compounds may be used singly or in plural combinations within the range 0.01 to 2% by mass relative to 100% by mass of base oil.

As examples of the aforementioned phosphate esters, mention may be made of tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triheptyl phosphate, trioctyl phosphate, trinonyl phosphate, tridecyl phosphate, triundecyl phosphate, tridodecyl phosphate, tritridecyl phosphate, tritetradecyl phosphate, tripentadecyl phosphate, trihexadecyl phosphate, triheptadecyl phosphate, trioctadecyl phosphate, trioleyl phosphate, triphenyl phosphate, tris(iso-propylphenyl)phosphate, triallyl phosphate, tricresyl phosphpate, trixylenyl phosphate, cresyldiphenyl phosphate and xylenyldiphenyl phosphate.

As specific examples of the aforementioned acidic phosphate esters, mention may be made of monobutyl acid

phosphate, monopentyl acid phosphate, monohexyl acid phosphate, monoheptyl acid phosphate, monooctyl acid phosphate, monononyl acid phosphate, monodecyl acid phosphate, monoundecyl acid phosphate, monododecyl acid phosphate, monotridecyl acid phosphate, monotetradecyl acid phosphate, monopentadecyl acid phosphate, monohexadecyl acid phosphate, monoheptadecyl acid phosphate, monooctadecyl acid phosphate, monooleyl acid phosphate, dibutyl acid phosphate, dipentyl acid phosphate, dihexyl acid phosphate, diheptyl acid phosphate, dioctyl acid phosphate, dinonyl acid phosphate, didecyl acid phosphate, diundecyl acid phosphate, didodecyl acid phosphate, ditridecyl acid phosphate, ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate, dioctadecyl acid phosphate and dioleyl acid phosphate.

As examples of the aforementioned amine salts of acidic phosphate esters, mention may be made of the methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine and trioctylamine salts of the previously mentioned acidic phosphate esters.

As examples of the aforementioned phosphite esters, mention may be made of dibutyl phosphite, dipentyl phosphite, dihexyl phosphite, diheptyl phosphite, dioctyl phosphite, dinonyl phosphite, didecyl phosphite, diundecyl phosphite, didoecyl phosphite, dioleyl phosphite, diphenyl phosphite, dicresyl phosphite,

tributyl phosphite, tripentyl phosphite, trihexyl phosphite, triheptyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, triundecyl phosphite, tridodecyl phosphite, trioleyl phosphite, triphenyl phosphite and tricresyl phosphite.

As examples of the aforementioned zinc dithiophosphates, mention may be made in general of zinc dialkyl dithiophosphates, zinc diaryl dithiophosphates and zinc arylalkyl dithiophosphates. For example, zinc dialkyl dithiophosphates where the alkyl groups of the zinc dialkyl dithiophosphates have primary or secondary alkyl groups of 3 to 22 carbons or alkylaryl groups substituted with alkyl groups of 3 to 18 carbons may be used. As specific examples of zinc dialkyl dithiophosphates, mention may be made of zinc dipropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc dipentyl dithiophosphate, zinc dihexyl dithiophosphate, zinc diisopentyl dithiophosphate, zinc diethylhexyl dithiophosphate, zinc dioctyl dithiophosphate, zinc dinonyl dithiophosphate, zinc didecyl dithiophosphate, zinc didoecyl dithiophosphate, zinc dipropylphenyl dithiophosphate, zinc dipentylphenyl dithiophosphate, zinc dipropylmethylphenyl dithiophosphate, zinc dinonylphenyl dithiophosphate and zinc didodecylphenyl dithiophosphate.

In order to improve oiliness, it is possible to incorporate fatty acid esters of polyhydric alcohols in the lubricating oil composition of this invention. For example, it is possible to use partial or complete esters of saturated or unsaturated fatty acids having 1 to 24 carbons and polyhydric alcohols such as glycerol, sorbitol, alkylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol and xylidol.

As examples of glycerol esters, mention may be made of glycerol monolaurylate, glycerol monostearate, glycerol monopalmitate, glycerol monooleate, glycerol dilaurylate, glycerol distearate, glycerol dipalmitate and glycerol dioleate.

For sorbitol esters mention may be made of sorbitol monolaurylate, sorbitol monopalmitate, sorbitol monostearate, sorbitol monooleate, sorbitol dilaurylate, sorbitol dipalmitate, sorbitol distearate, sorbitol dioleate, sorbitol tristearate, sorbitol trilaurylate, sorbitol trioleate and sorbitol tetraoleate.

Alkylene glycol esters include ethylene glycol monolaurylate, ethylene glycol monostearate, ethylene glycol monooleate, ethylene glycol dilaurylate, ethylene glycol distearate, ethylene glycol dioleate, propylene glycol monolaurylate, propylene glycol monostearate, propylene glycol monooleate, propylene glycol dilaurylate, propylene glycol distearate and propylene glycol dioleate.

For neopentyl glycol esters mention may be made of neopentyl glycol monolaurylate, neopentyl glycol monostearate, neopentyl glycol monooleate, neopentyl glycol dilaurylate, neopentyl glycol distearate and neopentyl glycol dioleate.

Trimethylolpropane esters include trimethylolpropane monolaurylate, trimethylolpropane monostearate, trimethylolpropane monooleate, trimethylolpropane dilaurylate, trimethylolpropane distearate, trimethylolpropane dioleate and trimethylolpropane monolaurylate.

Pentaerythritol esters include pentaerythritol monostearate, pentaerythritol monooleate, pentaerythritol dilaurylate, pentaerythritol distearate, pentaerythritol

dioleate and dipentaerythritol monooleate. For such fatty acid esters of polyhydric alcohols it is preferable to use partial esters of polyhydric alcohols and unsaturated fatty acids.

In order to enhance oxidative stability, it is possible to incorporate anti-oxidants in this invention. For the anti-oxidants, those used in lubricating oils are preferred for practical use, and mention may be made of phenolic anti-oxidants, aromatic amine-based anti-oxidants, sulphur-based anti-oxidants and phosphorus-based anti-oxidants. These anti-oxidants may be used singly or in plural combinations within the range of 0.01 to 5% by mass relative to 100% by mass of base oil.

As examples of the aforementioned aromatic amine-based anti-oxidants, mention may be made of dialkyl-diphenylamines such as p,p'-dioctyl-diphenylamine (Nonflex OD-3, made by Seiko Chemical Ltd), p,p'-di-α-methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butyldiphenylamine and monooctyldiphenylamine, bis(dialkylphenyl)amines such as di(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octyl-phenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as Phenothiazine (made by Hodogaya Chemical Ltd.) and 3,7-dioctylphenothiazine.

Phenolic anti-oxidants include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-

butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone (Antage DBH, made by Kawaguchi Chemical Industry Co. Ltd.), 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, and 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol.

Also, there are 3,5-di-t-butyl-4-hydroxybenzylmercapto-octylacetate, alklyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate (Yoshinox SS, made by Yoshitomi Fine Chemicals Ltd.), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-C7-C9 side-chain alkyl esters (Irganox L135, made by Ciba Specialty Chemicals Ltd.), 2,6-di-t-butyl-α-dimethylamino-p-cresol, and 2,2'-methylenebis(4-alkyl-6-t-butylphenol)s such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (Antage W-400, made by Kawaguchi Chemical Industry Ltd.) and 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (Antage W-500, made by Kawaguchi Chemical Industry Ltd).

Furthermore, there are bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (Antage W-300, made by Kawaguchi Chemical Industry Ltd.), 4,4'-methylenebis(2,6-di-t-butylphenol) (Ionox 220AH, made by Shell Japan Ltd.), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A, made by Shell Japan Ltd.), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethylene glycol bis[3-(3,5-di-t-butyl-

4-hydroxyphenyl)propionate] (Irganox L109, made by Ciba Specialty Chemicals Ltd.), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (Tominox 917, made by Yoshitomi Fine Chemicals Ltd.), 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (Irganox L115, made by Ciba Specialty Chemicals Ltd.), 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane (Sumilizer GA80, made by Sumitomo Chemicals), 4,4'-thiobis(3-methyl-6-t-butylphenol) (Antage RC, made by Kawaguchi Chemical Industry Ltd.) and 2,2'-thiobis(4,6-di-t-butyl-resorcinol).

Mention may also be made of polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]methane (Irganox L101, made by Ciba Specialty Chemicals Ltd.), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (Yoshinox 930, made by Yoshitomi Fine Chemicals Ltd.), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (Ionox 330, made by Shell Japan Ltd.), bis-[3,3'-bis-(4'-hydroxy-3'-t-butylphenyl) butyric acid] glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl) methyl-4-(2'',4''-di-t-butyl-3''-hydroxyphenyl)methyl-6-t-butylphenol and 2,6,-bis(2'-hydroxy-3'-t-butyl-5'-methyl-benzyl)-4-methylphenol, and phenol-aldehyde condensates such as condensates of p-t-butylphenol and formaldehyde and condensates of p-t-butylphenol and acetaldehyde.

As examples of sulphur-based anti-oxidants, mention may be made of dialkyl sulphides such as didodecyl sulphide and dioctadecyl sulphide, thiodipropionate esters such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and

dodecyloctadecyl thiodipropionate, and 2-mercaptobenzoimidazole.

As examples of phosphorus-based anti-oxidants mention may be made of triarylphosphites such as triphenylphosphite and tricresylphosphite, trialkylphosphites such as trioctadecylphosphite and tridecylphosphite, and tridodecyltrithiophosphite.

Additives to prevent metallic corrosion can be incorporated in this invention with a view to reinforcing compatibility with metallic materials. Metal deactivators that can be used together with the composition of this invention include benzotriazole and benzotriazole derivatives which are 4-alkyl-benzotriazoles such as 4-methyl-benzotriazole and 4-ethyl-benzotriazole, 5-alkyl-benzotriazoles such as 5-methyl-benzotriazole and 5-ethyl-benzotriazole, 1-alkyl-benzotriazoles such as 1-dioctylaminomethyl-2,3-benzotriazole and 1-alkyl-tolutriazoles such as 1-dioctylaminomethyl-2,3-tolutriazole, and benzoimidazole and benzoimidazole derivatives which are 2-(alkyldithio)-benzoimidazoles such as 2-(octyldithio)-benzoimidazole, 2-(decyldithio)-benzoimidazole and 2-(dodecyldithio)-benzoimidazole and 2-(alkyldithio)toluimidazoles such as 2-(octyldithio)-toluimidazole, 2-(decyldithio)-toluimidazole and 2-(dodecyldithio)toluimidazole.

Also, mention may be made of indazole, indazole derivatives which are toluindazoles such as 4-alkyl-indazoles and 5-alkyl-indazoles, benzothiazole, and benzothiazole derivatives which are 2-mercaptobenzothiazole derivatives (Thiolite B-3100, made by Chiyoda Chemical Industries Ltd.), 2-(alkykldithio)benzothiazoles such as 2-(hexyldithio)benzothiazole and 2-

(octyldithio)benzothiazole, 2-(alkyldithio)toluthiazoles such as 2-(hexyldithio)toluthiazole and 2-(octyldithio)toluthiazole, 2-(N,N-dialkylydithiocarbamyl)-benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)-benzothiazole, 2-(N,N-dibutyldithiocarbamyl)-benzothiazole and 2-(N,N-dihexyldithiocarbamyl)-benzothiazole, and 2-(N,N-dialkylydithiocarbamyl)-toluzothiazoles such as 2-(N,N-diethyldithiocarbamyl)-toluthiazole, 2-(N,N-dibutyldithiocarbamyl)-toluthiazole and 2-(N,N-dihexyldithiocarbamyl)-toluthiazole.

Further, mention may be made of benzooxazole derivates which are 2-(alkyldithio)benzooxazoles such as 2-(octyldithio)benzooxazole, 2-(decyldithio)benzooxazole and 2-(dodecyldithio)benzooxazole or which are 2-(alkyldithio)toluoxazoles such as 2-(octyldithio)toluoxazole, 2-(decyldithio)toluoxazole and 2-(dodecyldithio)toluoxazole, thiadiazole derivatives which are 2,5-bis(alkyldithio)-1,3,4-thiadiazoles such as 2,5-bis(heptyldithio)-1,3,4-thiadiazole, 2,5-bis(nonyldithio)-1,3,4-thiadiazole, 2,5-bis(dodecyldithio)-1,3,4-thiadiazole and 2,5-bis(octadecyldithio)-1,3,4-thiadiazole, 2,5-bis(N,N-dialkyldithiocarbamyl)-1,3,4-thiadiazoles such as 2,5-bis(N,N-diethyldithiocarbamyl)-1,3,4-thiadiazole, 2,5-bis(N,N-dibutyldithiocarbamyl)-1,3,4-thiadiazole and 2,5-bis(N,N-dioctyldithiocarbamyl)-1,3,4-thiadiazole and 2-N,N-dialkyldithiocarbamyl-5-mercapto-1,3,4-thiadiazoles such as 2-N,N-dibutyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole and 2-N,N-dioctyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole, and triazole derivates which are, for example, 1-alkyl-2,4-triazoles such as 1-di-octylaminomethyl-2,4-triazole.

These metal deactivators may be used singly or in plural combinations within the range 0.01 to 0.5% by mass relative to 100% by mass of base oil.

In order to improve performance further, it is possible where necessary to make appropriate use of various additives other than those aforementioned. As examples of these, mention may be made of defoaming agents, viscosity index improvers, pour-point depressants, detergent dispersants, rust preventatives, demulsifying agents, and other known lubricating oil additives.

In order to improve the low-temperature flow characteristics and viscosity characteristics, pour-point depressants and viscosity-index improvers can also be added to the lubricating oil composition of this invention. As examples of viscosity-index improvers mention may be made of non-dispersant type viscosity-index improvers such as polymethacrylates and olefin polymers such as ethylene-propylene copolymers, styrene-diene copolymers, polyisobutylene and polystyrene, and dispersant type viscosity-index improvers where nitrogen-containing monomers have been copolymerised with these. As regards the amount to be added, they may be used within the range 0.05 to 20% by mass relative to 100% by mass of base oil. As examples of pour-point depressants mention may be made of polymethacrylate-based polymers. As regards the amount to be added, they may be used within the range 0.01 to 5% by mass relative to 100% by mass of base oil.

Defoaming agents may also be added in order to impart defoaming characteristics to the lubricating oil composition of this invention. As examples of defoaming agents suitable for this invention, mention may be made

of organosilicates such as dimethylpolysiloxane, diethylsilicate and fluorosilicone, and non-silicone type defoaming agents such as polyalkylacrylates. As regards the amount to be added, they may be used singly or in plural combinations within the range of 0.0001 to 0.1% by mass relative to 100% by mass of base oil.

As examples of demulsifiers suitable for this invention, those in the known art normally used as additives for lubricating oils can be used. As regards the amount to be added, they may be used within the range of 0.0005 to 0.5% by mass relative to 100% by mass of base oil.

Examples

The invention is explained in specific detail below by means of Examples and Comparative Examples, but the invention is not limited to only these forms of embodiment.

For preparation of the Examples and Comparative Examples, the compositions and materials mentioned below were used.

1. (1-1) Base oil: A paraffinic mineral oil obtained by appropriate use of a suitable combination of refining processes such as hydrocracking and dewaxing in respect of a lubricating oil fraction obtained by atmospheric distillation of crude oil, and classified as Group II according to the API (American Petroleum Institute) base oil classification. (Characteristics: kinematic viscosity at 100°C (ASTM D445), 5.35 mm^2/s; kinematic viscosity at 40°C (ASTM D445), 31.4 mm^2/s; viscosity index (ASTM D2270), 103; 15°C density, 0.864; sulphur content (as converted to elemental sulphur), less than 10 ppm; nitrogen content (as converted to elemental nitrogen), less than 1 ppm; aniline point, 110°C; ring-analysis

paraffin content according to the method of ASTM D3238, 62%; naphthene content ditto, 38%; aromatic content ditto, less than 1%; initial boiling point temperature according to gas chromatography distillation by the method of ASTM D5480, 312°C)

(1-2)Base Oil 2: A GTL base oil synthesised by the Fischer-Tropsch method, and classified as Group III according to the API (American Petroleum Institute) base oil classification. (Characteristics: kinetic viscosity at 100°C, 5.10 mm2/s; kinetic viscosity at 40°C, 23.5 mm2/s; viscosity index, 153; 15°C density, 0.821; sulphur content (as converted to elemental sulphur), less than 10 ppm; nitrogen content (as converted to elemental nitrogen), less than 1 ppm; ring-analysis aromatic content according to the method of ASTM D3238, less than 1%)

2. Additives

(2-1) Additive A: Aspartic acid derivative: a mixture of N-1-oxo-3-carbonyloxypropyl-N-3-octyloxypropyl-diisobutyl aspartate ester, N-1-oxo-3-carbonyloxypropyl-N-3-decyloxypropyl-diisobutyl aspartate ester, N-1-oxo-3-carbonyloxypropyl-N-3-dodecyloxypropyl-diisobutyl aspartate ester and N-1-oxo-3-carbonyloxypropyl-N-3-tetradecyloxypropyl-diisobutyl aspartate ester (acid number by the method of JIS K2501: 100 mgKOH/g)

(2-2) Additive B: Succinic acid derivative: tetrapropenyl succinic acid, 1,3-propanediol half ester (acid number by the method of JIS K2501: 160 mgKOH/g)

(2-3) Additive C1: Thiophosphate ester compound: 3-(di-isobutoxy-thiophosphorylsulphanyl)-2-methyl-propionic acid (acid number by the method of JIS K2501: 160 mgKOH/g)

(2-4) Additive C2: Thiophosphate ester compound: ethyl-3-[[bis-(1-methylethoxy)phosphinothioyl]thio] propionate (acid number by the method of JIS K2501: 9.6 mgKOH/g)

(2-5) Additive D1: N-alkenyl diethanolamine (the main constituent being N-oleyl diethanolamine); tertiary amine compound (base number by the method of JIS K2501: 160 mgKOH/g)

(2-6) Additive D2: isostearic acid triethylene tetramide (base number by the method of JIS K2501: 7.2 mgKOH/g)

(2-7) Additive D3: ester : pentaerythritol oleate (major content: pentaerythritol dioleate)(JIS K0070 hydroxy value : 200mgKOH/g)

Examples 1 to 6, Comparative Examples 1 to 4

Using the aforementioned compositions and materials, the lubricating compositions of Examples 1 to 2 and Comparative Examples 1 to 4 were prepared with the constitutions shown in Tables 1 to 3.

Tests

The following tests were carried out on the lubricating compositions of the aforementioned Examples 1 to 2 and Comparative Examples 1 to 4 in order to observe their performance.

Rust Prevention Tests

Following JIS K2510, 300 ml of test oil was taken and put in a container installed in a constant-temperature bath. It was agitated at a speed of 1000 turns per minute. When the temperature reached 60°C, an iron test specimen was inserted into the oil and 30 ml of artificial sea water was also added. Keeping the temperature at 60°C, agitation was continued for 24 hours. Then the specimen was removed and assessed

visually for occurrence of any rust. If no rust appeared, a pass was awarded.

FZG Gear Test

Pursuant to ASTM D5182, FZG Gear TEST was carried out.

This twister test measure the scuffing (adhesive wear) load capacity, more specifically extreme pressure property, of a lubricating oil using a pair of spur gear.

Fail-stage means to happen the damage (scuffing) of gear tooth.

Fail-stage 1 means to happen the damage of gear tooth by 99N (Load), similarly, Fail-stage 2 is 407N (Load), Fail-stage 3 is 1044N (Load), Fail-stage 4 is 1799N (Load), Fail-stage 5 is 2786N (Load), Fail-stage 6 is 4007N (Load), Fail-stage 7 is 5435N (Load), Fail-stage 8 is 7080N (Load), Fail-stage 9 is 8949N (Load), Fail-stage 10 is 11029N (Load), Fail-stage 11 is 13342N (Load), Fail-stage 12 is 15826N (Load).

Over-stage 12 (Pass 12) means to pass, no occurrence of damage of gear tooth by, maximum loading state 12 in this test.

A lubricating oil having high fail-stage shows excellent extreme pressure property.

Pass-Lubricating-oil is hydraulic fluid for construction machine more than Fail-stage 8 determined by JCMAS (Japan Construction Mechanization Association).

Shell Four-ball Load-resistance Capacity Test

Following the test method of the Japan Petroleum Society's standard (JPI-5S-40-93) and using a Shell four-ball load-resistance capacity test rig, the last non-seizure load (LNL) and weld load (WL) of the test oils were measured. Those with high load values in the test results excelled in extreme-pressure properties.

Test Results

The results of the tests are shown in Tables 1 and 2.

Discussion

Examples 1 and 2, because of the joint use of the aspartic acid derivative (Additive A) and the succinic acid derivative (Additive B), had good rust-preventing properties despite the fact that the amounts added, being 0.03% by mass in total, were small. In the case of Example 1, fail stage of FZG gear test was 12, the extreme-pressure additive (Additive C1) was effective and excellent extreme-pressure properties were displayed, with the last non-seizure load (LNL) being 100 kgf and the weld load (WL) 160 kgf. In Example 2 using GTL (base oil), fail-stage of FZG gear test was over 12, it showed more effective extreme-pressure property. In the case of Example 3, also, where a different extreme-pressure agent (Additive C2) was used, the same good extreme-pressure properties were obtained. It was thus evident that a lubricating composition with superior rust-preventing and extreme-pressure properties had been obtained through small amounts of aspartic acid derivative, succinic acid derivative and thiophosphate ester used at the same time.

In Examples 4, 5 and 6, in which a aspartic acid derivative (Additive A), a succinic acid derivative (Additive B), and one agent selected from amine compound (Additive D1), amide compound (Additive D2), or ester compound (Additive D3) were used in combination, excellent anti-rust property and excellent extreme pressure property were shown.

On the other hand, when using an aspartic acid derivative (Additive B) alone as in the cases of Comparative Examples 1 and 2, although good rust-

preventing properties were eventually obtained when the amount of aspartic acid derivative was blended in at more than 5.3 times the case of Example 1, at 0.08% by mass, even with the same use of Additive C1 the extreme-pressure properties were still lower than in Example 1, fail stage of FZG gear test was 7, the last non-seizure load (LNL) was 80 kgf and the weld load (WL) 126 kgf according to Shell Four Ball Test.

Also, when using a succinic acid derivative (Additive B) alone as in the cases of Comparative Examples 3 and 4, although good rust-preventing properties were eventually obtained when the amount of succinic acid derivative was blended in at no less than 4.6 times the case of Example 1, at 0.07% by mass, even with the same use of Additive C1 the extreme-pressure properties were still lower than in Example 1, the fail stage of FZG gear test was 4, the last non-seizure load (LNL) according to Shell Four Ball Test was 63 kgf and the weld load (WL) according to Shell Four Ball Test 126 kgf.

Since rust occurred in the cases of Comparative Examples 1 and 3, no FZG gear test and no Shell four-ball load-resistance capacity test was carried out.

Table 1

		Example 1	Example 2	Example 3
Composition	Base Oil, Gp II	99.95		99.77
	Base Oil, GTL		99.95	
	Additive A: aspartic acid derivative	0.015	0.015	0.015
	Additive B: Succinic acid derivative	0.015	0.015	0.015
	Additive C1: 3-(di-isobutoxy-thiophosphoryl sulphanyl)-2-methyl-propionic acid	0.02	0.02	
	Additive C2: ethyl-3-[[bis-(1-methylethoxy)phosphinothioyl]thio] propionate			0.2
Test Results	Rust (artificial sea water)	Pass	Pass	Pass
	FZG (fail stage)	12	≥ 12	9
	Last non-seizure load (LNL) (kgf)	100	100	80
	Weld load (WL) (kgf)	160	160	160

Table 2

		Example 4	Example 5	Example 6
Composition	Base Oil, Gp II	99.900	99.850	99.850
	Additive A: aspartic acid derivative	0.015	0.015	0.015
	Additive B: Succinic acid derivative	0.015	0.015	0.015
	Additive C1: 3-(di-isobutoxy-thiophosphoryl sulphanyl)-2-methyl-propionic acid	0.020	0.020	0.020
	Additive D1: N-alkenyl diethanolamine (major content N-oleyl diethanolamine)	0.050		
	Additive D2: isostearic acid triethylene tetramide		0.100	
	Additive D3: ester : pentaerythritol oleate (major content: pentaerythritol dioleate)			0.100
Test Results	Rust (artificial sea water)	Pass	Pass	Pass
	FZG (fail stage)	8	9	11

Table 3

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Composition	Base Oil, Gp II	99.92	99.90	99.98	99.91
	Additive A: aspartic acid derivative	0.07	0.08		
	Additive B: Succinic acid derivative			0.06	0.07
	Additive C1: 3-(di-isobutoxy-thiophosphoryl sulphanyl)-2-methyl-propionic acid	0.02	0.02	0.02	0.02
Test Results	Rust (artificial sea water)	Fail	Pass	Fail	Pass
	FZG (fail stage)		7		4
	Last non-seizure load (LNL) (kgf)	---	80	---	63
	Weld load (WL) (kgf)	---	126	---	126

C L A I M S

1. A lubricating composition comprising a base oil, an aspartic acid derivative, a succinic acid derivative and a thiophosphate ester.

2. A lubricating composition according to Claim 1 containing, relative to the total amount of the composition, from 0.001 to 0.5% by mass of the aspartic acid derivative, from 0.001 to 0.5% by mass of the succinic acid derivative and from 0.001 to 1% by mass of the thiophosphate ester.

3. A lubricating composition according to Claim 1 or 2, wherein the acid number of the aspartic acid derivative is from 10 to 200 mgKOH/g.

4. A lubricating composition according to any of Claims 1 - 4 wherein the acid number of the succinic acid derivative is from 10 to 300 mgKOH/g.

5. A lubricating composition according to any of Claims 1 - 4 wherein the thiophosphate ester is a β-dithiophosphoryl carboxylic acid derivative.

6. A lubricating composition according to any of Claims 1 - 5 wherein the base oil comprises a synthetic oil.

7. A lubricating composition according to Claim 6 wherein the synthetic oil comprises a poly-α-olefin.

8. A lubricating composition according Claim 6 wherein the synthetic oil comprises a GTL-derived base oil.

9. A lubricating composition according to any of Claims 1 - 8, further containing at least one compound selected from an amine compound, amide compound and ester compounds.

10. A lubricating composition according to Claims 9, wherein the one compound selected from amine compound, amide compound, and ester compound, is an aliphatic amine compound and/or amide compound, and the aliphatic carbon number is 1 to 30, or ester compound and the aliphatic carbon number is 6 to 30.

11. Use of the lubricating composition according to any of Claims 1 - 10 for improving one or more of rust-prevention and extreme-pressure properties.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/067365

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M141/06 C10M169/04
ADD. C10N20/02 C10N30/06 C10N30/12 C10N40/02 C10N40/04
C10N40/06 C10N40/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/214733 A1 (BABA YOSHIHARU [JP]) 28 October 2004 (2004-10-28) paragraphs [0031], [0033], [0034], [0057]; examples	1-11
X	US 3 687 852 A (GODFREY ARTHUR WILLIAM ET AL) 29 August 1972 (1972-08-29) column 7, lines 1-28	1-4,9,10
X	EP 0 434 464 A (ETHYL PETROLEUM ADDITIVES LTD [GB]) 26 June 1991 (1991-06-26) page 3, columns 38-40; table 1	1-11
X	US 4 834 892 A (DAMIN BERNARD [FR] ET AL) 30 May 1989 (1989-05-30) examples 1-3; table 1	1-11

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 March 2009	03/04/2009

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/067365

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 852 205 A (KABLAOUI M ET AL) 3 December 1974 (1974-12-03) table 1	1,3,4,9, 10

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