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(54) Title: LUBRICATING OIL COMPOSITION

(57) Abstract: Lubricating oil composition characterised in that it incorporates as additives in a mineral oil and/or synthetic oil base oil a succinic acid derivative and an alkanolamine compound. The lubricating oil composition of the present invention is suitable as an industrial lubricating oil and has good rust preventing properties, a reduced friction coefficient and excellent energy saving characteristics.



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LUBRICATING OIL COMPOSITION

Field of the Invention

This invention relates to lubricating oil compositions and generally to industrial lubricating oils using refined base oils. In particular it relates to lubricating oil compositions used as machine oils, hydraulic oils, turbine oils, compressor oils, gear oils and bearing oils.

Background of the Invention

Good rust-preventing properties and friction characteristics are required of lubricating oil compositions, and among them industrial lubricating oil compositions. The requirement is to reduce friction losses efficiently in mechanical apparatus and to achieve large energy economies through having a low friction coefficient (μ).

For example, hydraulic apparatus is widely used in construction machinery and so on, and if the friction coefficient of the lubricating oil used for the hydraulic oil actuating the machinery is high, the phenomenon of minute stick-slip may occur in the sliding friction parts of the packing owing to the reciprocating movement of the hydraulic cylinders, and chatter, vibration, squealing and other abnormal sounds may occur in the cylinders, so that it becomes impossible to control the hydraulic plant with satisfactory precision (Japanese Laid-open Patent H9-111277 (1997)). In consequence it is necessary to reduce the friction coefficient of the lubricating oil so that the hydraulic cylinders move smoothly and accurately.

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 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.

This invention is intended to obtain an industrial lubricating oil which reduces the friction coefficient exhibited by the lubricating oil and which has high energy-saving properties. If such a lubricating oil composition is used as a hydraulic oil in hydraulic apparatus, it is also intended to make it possible to control the hydraulic apparatus with precision and without giving rise to chatter, vibration, squealing and other abnormal sounds in the cylinders, as well as inhibiting the occurrence of rust and imparting good corrosion resistance. By these means it is intended to obtain a lubricating oil composition that has good rust-preventing properties, that is well endowed with energy-saving properties because of low friction characteristics, and that has good operating efficiency.

Summary of the Invention

According to the present invention there is provided a lubricating oil composition characterised in that it incorporates as additives in a mineral oil and/or synthetic oil base oil a succinic acid derivative and an alkanolamine compound.

By adding, as additives, a succinic acid derivative and an alkanolamine compound to a base oil which is a mineral oil or a synthetic oil, or a mixture thereof, this invention makes it possible to obtain an industrial

lubricating oil composition which is well endowed with rust-preventing properties, which has excellent energy-saving properties, and which is suitable as a hydraulic oil.

5 According to this invention, it is possible to reduce effectively the friction losses that occur in various kinds of industrial apparatus, and to bring about energy savings. Also, if it is used as a hydraulic oil, it is possible, by reducing the friction coefficient, to
10 make it possible to control the hydraulic apparatus with precision and without giving rise to chatter, vibration, squealing and other abnormal sounds in the cylinders. In addition, it is possible to inhibit the occurrence of rust and to obtain a lubricating oil composition well
15 endowed with rust-preventing properties.

Detailed Description of the Invention

For the base oil of the present lubricating oil composition it is possible to use mineral oils and synthetic oils normally used for lubricating oils, and in
20 particular it is possible to use, singly or as mixtures, base oils which belong to Group I, Group II, Group III and Group IV of the API (American Petroleum Institute) base oil categories.

Group I base oils include, for example, paraffinic
25 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 should be
30 in the range of from 80 to 120 and preferably in the range of from 95 to 110. The kinematic viscosity at 40°C should preferably be in the range of from 2 to 680 mm²/s and even more preferably in the range of from 8 to 220

mm²/s. The total nitrogen content should be less than 50 ppm and preferably less than 25 ppm. In addition, oils with an aniline point in the range of from 80 to 150°C and preferably in the range of from 90 to 120°C should be used.

Group II base oils include, for example, paraffinic mineral oils obtained by appropriate use of a suitable combination of refining processes such as hydrotreating and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil. Group II base oils refined by hydrotreating 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 should be in the range of from 90 to 125 and preferably in the range of from 100 to 120. The kinematic viscosity at 40°C should preferably be in the range of from 2 to 680 mm²/s and even more preferably in the range of from 8 to 220 mm²/s. Also, the total sulphur content should be less than 700 ppm, preferably less than 100 ppm and even more preferably less than 10 ppm. The total nitrogen content should be less than 10 ppm and preferably less than 1 ppm. In addition, oils with an aniline point in the range of from 80 to 150°C and preferably in the range of from 100 to 135°C should be used.

Suitable Group III and Group II+ base oils include paraffinic mineral oils manufactured by a high degree of hydrotreating in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil, base oils refined by Isodewaxing which dewaxes and substitutes the wax produced by the dewaxing process with

isoparaffins, and base oils refined by the Mobil wax isomerisation process. The viscosity of these base oils is not specially limited, but the viscosity index should be in the range of from 95 to 145 and preferably in the range of from 100 to 140. The kinematic viscosity at 40°C should preferably be in the range of from 2 to 680 mm²/s and even more preferably in the range of from 8 to 220 mm²/s. Also, the total sulphur content should be in the range of from 0 to 100 ppm and preferably less than 10 ppm. The total nitrogen content should be less than 10 ppm and preferably less than 1 ppm. In addition, oils with an aniline point in the range of from 80 to 150°C and preferably in the range of from 110 to 135°C should be used.

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.

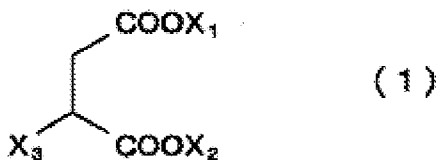
The aforementioned polyolefins include polymers of various olefins or hydrides thereof. Any olefin may be used, and as examples mention may be made of ethylene, propylene, butene and α -olefins with five or more carbons. In the manufacture of polyolefins, one kind of the aforementioned olefins may be 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 should preferably be in the range of from 2 to 680 mm²/s and more preferably in the range of from 8 to 220 mm²/s.

GTLs (gas to liquid) 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 should be in the range of from 130 to 180 and preferably in the range of from 140 to 175. Also, the kinematic viscosity at 40°C should be in the range of from 2 to 680 mm²/s and preferably in the range of from 5 to 120 mm²/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).

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, should be 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 succinic acid derivatives are shown in General Formula 1:



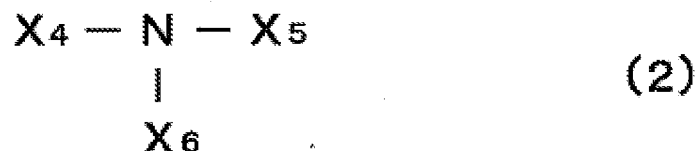
In the aforementioned General Formula 1, X₁ and X₂ are each hydrogen or alkyl groups, alkenyl groups or

hydroxyalkyl groups having from 3 to 6 carbon atoms which may be the same or different, and preferably should be hydrogen atoms, 1-hydroxypropyl groups, 2-hydroxypropyl groups, 2-methylpropyl groups or tertiary butyl groups. X_3 has from 1 to 30 carbon atoms and is an alkyl group or an alkenyl group, or an alkyl group having ether bonds, or a hydroxyalkyl group. Suitable, for example, are a methyl group, an ethyl group, a propyl group, a butyl group, a 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-($C_6 \sim C_{18}$)hydrocarboxy($C_3 \sim C_6$) 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-($C_{12} \sim C_{16}$)alkoxypropyl group.

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

As examples of the alkanolamine compounds in this

invention, mention may be made of the monoalkanolamine and dialkanolamine compounds shown in General Formula 2:



In the case where, in the aforementioned General Formula 2, out of X_4 , X_5 and X_6 one is a hydrogen atom and one of the others is an alkyl group or alkenyl group, and the last is a hydroxyalkyl group, in other words secondary amines of monoalcohols, as examples mention may be made of ethanol amines such as N-nonyl monoethanolamine, N-decyl monoethanolamine, N-undecyl monoethanolamine, N-lauryl monoethanolamine, N-tridecyl monoethanolamine, N-myristyl monoethanolamine, N-pentadecyl monoethanolamine, N-palmityl monoethanolamine, N-heptadecyl monoethanolamine, N-oleyl monoethanolamine, N-stearylamine monoethanolamine, N-isostearyl monoethanolamine, N-nonadecyl monoethanolamine, N-eicosyl monoethanolamine, N-coconut monoethanolamine, N-beef tallow monoethanolamine, N-hydrogenated beef tallow monoethanol amine and N-soybean monoethanolamine.

Also, mention may be made of propanol amines such as N-nonyl monopropanolamine, N-decyl monopropanolamine, N-undecyl monopropanolamine, N-lauryl monopropanolamine, N-tridecyl monopropanolamine, N-myristyl monopropanolamine, N-pentadecyl monopropanolamine, N-palmityl monopropanolamine, N-heptadecyl monopropanolamine, N-oleyl monopropanolamine, N-stearylamine monopropanolamine, N-isostearyl monopropanolamine, N-nonadecyl monopropanolamine, N-eicosyl monopropanolamine, N-coconut monopropanolamine, N-beef tallow

monopropanolamine, N-hydrogenated beef tallow
monopropanolamine and N-soybean monopropanolamine.

Further, in the case where, in the aforementioned
General Formula 2, out of X_4 , X_5 and X_6 two are alkyl
5 groups or alkenyl groups, and the other is a hydroxyalkyl
group, in other words tertiary amines of alcohols being
monoalkanolamines of the tertiary amine type, as examples
mention may be made of ethanol amines such as N-dinonyl
ethanolamine, N-didecyl ethanolamine, N-diundecyl
10 ethanolamine, N-dilauryl ethanolamine, N-ditridecyl
ethanolamine, N-dimyristyl ethanolamine, N-dipentadecyl
ethanolamine, N-dipalmityl ethanolamine, N-diheptadecyl
ethanolamine, N-dioleoyl ethanolamine, N-distearylamine
ethanolamine, N-diisostearyl ethanolamine, N-dinonadecyl
15 ethanolamine, N-dieicosyl ethanolamine, N-di-coconut
ethanolamine, N-di-beef tallow ethanolamine, N-di-
hydrogenated beef tallow ethanol amine and N-di-soybean
ethanolamine.

Also, mention may be made of propanol amines such as
20 N-dinonyl propanolamine, N-didecyl propanolamine, N-
diundecyl propanolamine, N-dilauryl propanolamine, N-
ditridecyl propanolamine, N-dimyristyl propanolamine, N-
dipentadecyl propanolamine, N-dipalmityl propanolamine,
N-diheptadecyl propanolamine, N-dioleoyl propanolamine, N-
25 distearylamine propanolamine, N-diisostearyl
propanolamine, N-dinonadecyl propanolamine, N-dieicosyl
propanolamine, N-di-coconut propanolamine, N-di-beef
tallow propanolamine, N-di-hydrogenated beef tallow
propanol amine and N-di-soybean propanolamine.



In the aforementioned General Formula 3, X_7 is an

alkyl group or an alkenyl group, and X₈ is a hydroxylalkyl group. As examples mention may be made of N-alkyl diethanol amines such as N-octyl diethanolamine, N-nonyl diethanolamine, N-decyl diethanolamine, N-undecyl
5 diethanolamine, N-lauryl diethanolamine, N-tridecyl diethanolamine, N-myristyl diethanolamine, N-pentadecyl diethanolamine, N-palmityl diethanolamine, N-heptadecyl diethanolamine, N-oleyl diethanolamine, N-stearylamine diethanolamine, N-isostearyl diethanolamine, N-nonadecyl
10 diethanolamine, N-eicosyl diethanolamine, N-coconut diethanolamine, N-beef tallow diethanolamine, N-hydrogenated beef tallow diethanol amine and N-soybean diethanolamine, and N-alkyl dipropanolamines such as N-octyl dipropanolamine, N-nonyl dipropanolamine, N-decyl
15 dipropanolamine, N-undecyl dipropanolamine, N-lauryl dipropanolamine, N-tridecyl dipropanolamine, N-myristyl dipropanolamine, N-pentadecyl dipropanolamine, N-palmityl dipropanolamine, N-heptadecyl dipropanolamine, N-oleyl dipropanolamine, N-stearylamine dipropanolamine, N-
20 isostearyl dipropanolamine, N-nonadecyl dipropanolamine, N-eicosyl dipropanolamine, N-coconut dipropanolamine, N-beef tallow dipropanolamine, N-hydrogenated beef tallow dipropanol amine and N-soybean dipropanolamine,

The alkanolamine compounds are used in the lubricating oil composition in an amount in the range of
25 from 0.001 to 1% by mass, but preferably in the range of from 0.001 to 0.8% by mass and more preferably in the range of from 0.005 to 0.5% by mass, relative to the mass of the lubricating composition. These compounds can
30 be used as one kind or as mixtures of several kinds.

It is possible to incorporate esters of polyhydric alcohols in the lubricating oil composition of this invention. As examples of such esters of polyhydric

alcohols used in the prior art as oiliness agents, it is possible to use partial or complete esters of saturated or unsaturated fatty acids having from 1 to 24 carbons of polyhydric alcohols such as glycerol, sorbitol, alkylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol and xylidol.

As specific examples of such, for 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, sorbitol sesquioleate 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, and trimethylolpropane dioleate.

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.

These fatty acid esters of polyhydric alcohols are used in the lubricating oil composition in an amount in the range of from 0.01 to 5% by mass, but preferably in the range of from 0.05 to 2% by mass, relative to the mass of the lubricating composition. If the amount used is outside the aforementioned range, the effect in reducing the friction coefficient may become weak.

In order to improve performance further, it is possible where necessary to make appropriate use of various kinds of additives other than the aforementioned constituents. As examples of these, mention may be made of anti-oxidants, metal deactivators, extreme pressure agents, oiliness improvers, defoaming agents, viscosity index improvers, pour-point depressants, detergent-dispersants, rust preventatives, demulsifying agents, and other lubricating oil additives of the known art.

For the anti-oxidants used in this invention, those used in lubricating oils are preferred for practical use, and mention may be made of phenol-based anti-oxidants, amine-based anti-oxidants and sulphur-based anti-oxidants. These anti-oxidants may be used singly or in plural combinations within the range of from 0.01 to 5%

by mass, relative to the mass of the lubricating oil composition.

As examples of the aforementioned 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-butyl-diphenylamine and mono-octyl-diphenylamine, 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.

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.

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.

5 Also, there are 3,5-di-t-butyl-4-hydroxybenzylmercapto-octylacetate, alkyl-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).

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

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-(alkyldithio)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-dialkyldithiocarbamyl)-benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)-benzothiazole, 2-(N,N-dibutyldithiocarbamyl)-benzothiazole and 2-(N,N-dihexyldithiocarbamyl)-benzothiazole, and 2-(N,N-dialkyldithiocarbamyl)-toluthiazoles 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 derivatives 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 derivatives 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 of from 0.01 to 0.5% by mass, relative to the mass of the lubricating oil composition.

It is possible also to add phosphorus compounds to the lubricating oil composition of this invention, and it is possible thereby to impart further anti-wear properties and extreme-pressure properties. As examples of phosphorus compounds suitable for this invention, mention may be made of phosphate esters, acidic phosphate esters, amine salts of acidic phosphate esters, phosphite esters, phosphorothionates, zinc dithiophosphates, esters of dithiophosphoric acid and alkanols or polyether-type

alcohols, and derivatives thereof, phosphorus-containing carboxylic acids and phosphorus-containing carboxylic acid esters.

5 These phosphorus compounds may be used singly or in plural combinations within the range of from 0.01 to 2% by mass, relative to the mass of the lubricating oil composition.

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

20 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
25 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
30 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
5 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,
10 dimethylamine, diethylamine, dipropylamine, dibutylamine,
dipentylamine, dihexylamine, diheptylamine, dioctylamine,
trimethylamine, triethylamine, tripropylamine,
tributylamine, tripentylamine, trihexylamine,
triheptylamine and trioctylamine salts of the previously
15 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,
20 diundecyl phosphite, didodecyl phosphite, dioleyl
phosphite, diphenyl phosphite, dicresyl phosphite,
tributyl phosphite, tripentyl phosphite, trihexyl
phosphite, triheptyl phosphite, trioctyl phosphite,
trinonyl phosphite, tridecyl phosphite, triundecyl
25 phosphite, tridodecyl phosphite, trioleyl phosphite,
triphenyl phosphite and tricresyl phosphite.

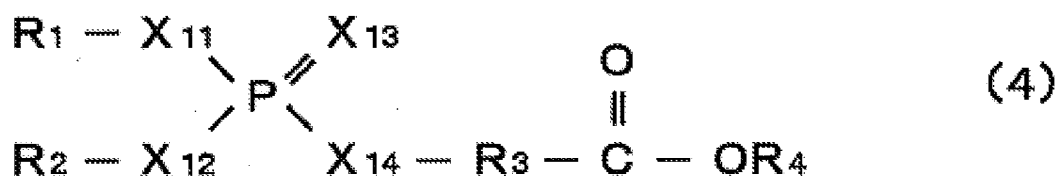
As examples of the aforementioned
phosphorothionates, mention may be made specifically of
tributyl phosphorothionate, tripentyl phosphorothionate,
30 trihexyl phosphorothionate, triheptyl phosphorothionate,
trioctyl phosphorothionate, trinonyl phosphorothionate,
tridecyl phosphorothionate, triundecyl phosphorothionate,
tridodecyl phosphorothionate, tritridecyl

phosphorothionate, tritetradecyl phosphorothionate,
tripentadecyl phosphorothionate, trihexadecyl
phosphorothionate, triheptadecyl phosphorothionate,
trioctadecyl phosphorothionate, trioleyl
5 phosphorothionate, triphenyl phosphorothionate, tricresyl
phosphorothionate, trixylenyl phosphorothionate,
cresyldiphenyl phosphorothionate, xylenyldiphenyl
phosphorothionate, tris(n-propylphenyl)
phosphorothionate, tris(isopropylphenyl)
10 phosphorothionate, tris(n-butylphenyl) phosphorothionate,
tris(isobutylphenyl) phosphorothionate, tris(s-
butylphenyl) phosphorothionate and tris(t-butylphenyl)
phosphorothionate. Mixtures of these may also be used.

As examples of the aforementioned zinc
15 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
20 alkyl groups having from 3 to 22 carbons or alkylaryl
groups substituted with alkyl groups having from 3 to 18
carbons may be used.

As specific examples of zinc dialkyl
dithiophosphates, mention may be made of zinc dipropyl
25 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,
30 zinc didodecyl dithiophosphate, zinc dipropylphenyl
dithiophosphate, zinc dipentylphenyl dithiophosphate,
zinc dipropylmethylphenyl dithiophosphate, zinc
dinonylphenyl dithiophosphate and zinc didodecylphenyl.

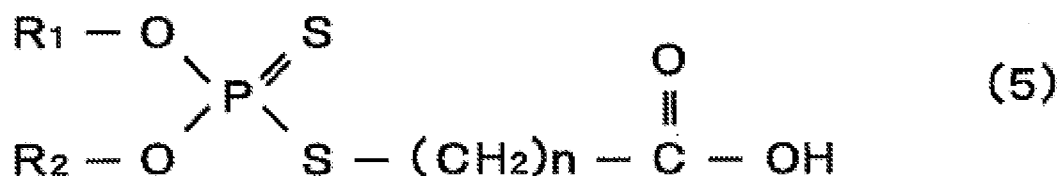
In the case of phosphorus-containing carboxylic acid compounds such as phosphorus-containing carboxylic acids and esters thereof, the molecules thereof should contain both a carboxyl group and a phosphorus atom. Their structure is not specially limited, but normally, from the standpoint of extreme-pressure properties and thermal and oxidative stability, phosphorylated carboxylic acids or phosphorylated carboxylic acid esters are preferred. As examples of phosphorylated carboxylic acids and phosphorylated carboxylic acid esters, mention may be made of compounds that can be expressed by the following General Formula (4).



In the aforementioned General Formula 4, R_1 and R_2 may be the same or different, and each denotes a hydrogen atom or a hydrocarbon group having from 1 to 30 carbons. R_3 denotes an alkylene group having from 1 to 20 carbons, R_4 denotes a hydrogen atom or a hydrocarbon group having from 1 to 30 carbons. X_{11} , X_{12} , X_{13} and X_{14} may be the same or different and each denotes oxygen atoms or sulphur atoms.

As examples of hydrocarbon groups having from 1 to 30 carbons in R₁ and R₂ of the aforementioned General Formula 4, mention may be made of alkyl groups, alkenyl groups, aryl groups, alkylaryl groups and arylalkyl groups.

Among the aforementioned phosphorylated carboxylic acids, the useful β -dithiophosphorylated propionic acids have the structure of the following General Formula (5).



As a specific example of these β -dithiophosphorylated propionic acids, mention may be made of 3-(di-isobutoxy-thiophosphorylsulphanyl)-2-methyl-propionic acid.

5 The amount of phosphorus-containing carboxylic acid compound in the present lubricating oil composition is not specially restricted, but is preferably in the range of from 0.001 to 1% by mass of the lubricating oil composition, and more preferably in the range of from
10 0.002 to 0.5% by mass, relative to the mass of the lubricating composition. If the content of phosphorus-containing carboxylic acid compound is less than the aforementioned lower limit, there will be a tendency for sufficient lubricity not to be achieved. On the other
15 hand, even if addition exceeds the aforementioned upper limit, there will be a tendency for an improving effect matching the content not to be achieved. Moreover, there is a risk that thermal and oxidative stability or
20 hydrolytic stability will decrease, which is not desirable.

Of the phosphorylated carboxylic acids expressed by the aforementioned General Formula (4), the amount of a compound where R_4 is a hydrogen atom is in the range of from 0.001 to 0.1% by mass, but preferably in the range
25 of from 0.002 to 0.08% by mass, more preferably in the range of from 0.003 to 0.07% by mass, yet more preferably in the range of from 0.004 to 0.06% by mass, and still more preferably in the range of from 0.005 to 0.05% by

mass, relative to the mass of the lubricating composition.

In order to improve the low-temperature flow characteristics and viscosity characteristics, pour-point depressants and viscosity-index improvers may 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 of from 0.05 to 20% by mass, relative to the mass of the lubricating oil composition.

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 of from 0.01 to 5% by mass, relative to the mass of the lubricating oil composition.

Defoaming agents may also be added in order to impart defoaming characteristics to the lubricating oil composition of this invention. As examples of such defoaming agents, 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 from 0.0001 to 0.1% by mass, relative to the mass of the lubricating oil composition.

As examples of demulsifiers suitable for this

invention, mention may be made of those in the known art normally used as additives for lubricating oils. As regards the amount to be added, they may be used within the range of from 0.0005 to 0.5% by mass, relative to the mass of the lubricating oil composition.

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 examples.

For preparation of the examples and comparative examples, the compositions and materials mentioned below were used.

1. Base oil (Gp II): 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, 5.35 mm²/s; kinematic viscosity at 40°C, 31.4 mm²/s; viscosity index, 103; 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 according to the method of ASTM D3238, 38%; aromatic content according to the method of ASTM D3238, less than 1%; initial boiling point temperature according to gas chromatography distillation by the method of ASTM D5480, 312°C).

2. Base Oil 2 (GTL5): 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. [Shell XHVI 5 (trade name)]

(Characteristics: kinematic viscosity at 100°C, 5.06 mm²/s; kinematic viscosity at 40°C, 23.6 mm²/s; viscosity index, 148; sulphur content (as converted to elemental sulphur), less than 10 ppm; nitrogen content (as converted to elemental nitrogen), less than 1 ppm; aniline point, 126°C; density at 15°C, 0.820; density at 20°C, 0.817; refraction index at 20°C, 1.456; initial boiling point temperature according to ASTM D5480 gas chromatography distillation, 365°C; 30% distillation point, 431°C; 50% distillation point, 460°C).

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

4. Additive B: N-alkenyl diethanolamine (main constituent N-oleyl diethanolamine); tertiary amine compound (base number by the method of JIS K2501: 160 mgKOH/g).

Examples 1 to 2, Comparative Examples 1 to 3

Lubricating oil compositions for Examples 1 and 2 and Comparative Examples 1 to 3 were prepared using the aforementioned materials in accordance with the compositions shown in Table 1. The amounts shown in Table 1 are in mass% unless otherwise specified.

Test Methods

The following test methods were carried out on the lubricating oil compositions of the aforementioned Examples 1 and 2 and Comparative Examples 1 to 3 in order to observe their performance.

Friction Coefficient

The friction coefficient was measured by means of a Masuda pendulum-type oiliness test rig made by Shinko

Engineering Co. Ltd. In this test, the test oil is supplied to the frictional part of the point of support of the pendulum, the pendulum is oscillated and the friction coefficient is obtained from the attenuation of the oscillations.

Evaluation of the tests was carried out using the following criteria:

Friction coefficient is not more than 0.135: Ø
(Excellent)

Friction coefficient is from 0.136 to under 0.150: O
(Good)

Friction coefficient is 0.150 or more: X (Not acceptable)

A smaller friction coefficient is preferred.

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.

Evaluation of the tests was carried out using the following criteria:

No rust O Pass

Occurrence of rust X Fail

Test results

The results of the various tests are shown in Table 1.

Discussion

As will be clear from the test results in Table 1,

in the case where a succinic acid derivative (Additive A) and an alkanolamine (Additive B) have been combined in Base Oil 1 as in Example 1, the friction coefficient was low at 0.117 and so was excellent (Ø), and there was no occurrence of rust in artificial sea water in the rust-preventing test, which was a pass (O).

In contrast, in the case of Base Oil 1 alone in Comparative Example 1, the friction coefficient was extremely high at 0.307 and not acceptable (X). Rust occurred in artificial sea water in the rust-preventing test, which was a fail (X). When a succinic acid derivative (Additive A) was added to Base Oil 1 as in Comparative Example 2, there was no occurrence of rust in artificial sea water in the rust-preventing test, which was a pass (O), but the friction coefficient was high at 0.159, which was not acceptable (X). Also, when an alkanolamine (Additive B) was added to Base Oil 1 as in Comparative Example 3, the friction coefficient was excellent (Ø), though was 0.122, and rust occurred in artificial sea water in the rust-preventing test, which was a fail (X). It was evident that superior results were obtained in Example 1.

Similarly good results were obtained in the case of Example 2 where the Base Oil 1 of Example 1 was replaced by Base Oil 2.

Table 1

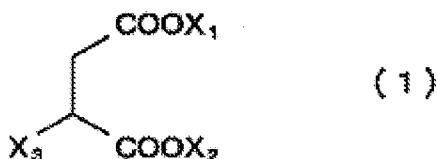
	Ex. 1	Ex. 2	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Composition	Base Oil 1	99.7		100	99.8
	Base Oil 2		99.7		
	Additive A Succinic acid derivative	0.1	0.1		0.1
	Additive B Alkanolamine	0.2	0.2		0.2
Test Results	Rust (artificial sea water)	Pass 0	Pass 0	Fail X	Fail X
	Pendulum test Friction coefficient	0.117 Ø	0.111 Ø	0.307 X	0.122 Ø

C L A I M S

1. Lubricating oil composition characterised in that it incorporates as additives in a mineral oil and/or synthetic oil base oil a succinic acid derivative and an alkanolamine compound.

2. Lubricating oil composition in accordance with Claim 1 wherein the acid number of the aforementioned succinic acid derivative is in the range of from 10 to 300 mgKOH/g (JIS K2501).

3. Lubricating oil composition in accordance with Claim 1 or Claim 2 wherein the succinic acid derivative is selected from compounds having the general formula (1)



wherein X_1 and X_2 are each hydrogen or alkyl groups, alkenyl groups or hydroxyalkyl groups having from 3 to 6 carbon atoms which may be the same or different, and preferably should be hydrogen atoms, 1-hydroxypropyl groups, 2-hydroxypropyl groups, 2-methylpropyl groups or tertiary butyl groups and X_3 has from 1 to 30 carbon atoms and is an alkyl group or an alkenyl group, or an alkyl group having ether bonds, or a hydroxyalkyl group.

4. Lubricating oil composition in accordance with any of Claims 1 to 3 wherein the aforementioned alkanolamine compound is a diethanolamine.

5. Lubricating oil composition in accordance with any of Claims 1 to 4 wherein the content in the lubricating oil composition of the aforementioned succinic acid

derivative is in the range of from 0.001 to 0.5% by mass.

6. Lubricating oil composition in accordance with any of Claims 1 to 5 wherein the content in the lubricating oil composition of the aforementioned alkanolamine

5 compound is in the range of from 0.001 to 1% by mass.

7. Lubricating oil composition in accordance with any of Claims 1 to 6 wherein the aforementioned base oil is a GTL base oil.

8. Use of the lubricating oil composition in accordance
10 with any of Claims 1 to 7 for improving rust-prevention properties.

9. Use of the lubricating oil composition in accordance with any of Claims 1 to 7 for reducing friction.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/052224

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10M141/06 C10M169/04
ADD. C10N30/06 C10N30/12

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	WO 2009/074664 A1 (SHELL INT RESEARCH [NL]; FUJIWARA AKIMITSU [JP]; NAGAKARI MITSUHIRO [J]) 18 June 2009 (2009-06-18) page 1 - page 3, line 13; claims; example 10	1-9
X	WO 2009/074667 A1 (SHELL INT RESEARCH [NL]; FUJIWARA AKIMITSU [JP]; KANEKO HIROSHI [JP];) 18 June 2009 (2009-06-18) page 1 - page 2; claims; example 4	1-9



Further documents are listed in the continuation of Box C.



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

29 April 2011

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06/05/2011

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/052224

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009074664	A1	18-06-2009	NONE
WO 2009074667	A1	18-06-2009	JP 2009161729 A
			23-07-2009