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## (54) LUBRICATING OIL COMPOSITION COMPRISING AN EPOXIDISED ESTER AND AN ASPARTIC ACID DERIVATIVE

SCHMIERÖLZUSAMMENSETZUNG, ENTHALTEND EINEN EPOXIDIERTEN ESTER UND EIN ASPARAGINSÄUREDERIVAT

COMPOSITION D'HUILE LUBRIFIANTE COMPRENANT UN ESTER ÉPOXYDÉ ET UN DÉRIVÉ D'ACIDE ASPARTIQUE

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## Description

**[0001]** The present invention provides lubricating oil compositions, and in particular lubricating oil compositions used as machine oils, hydraulic oils, turbine oils, compressor oils, gear oils, sliding friction oils, bearing oils and calibration oils.

**[0002]** Corrosion resistance is required as a fundamental property of lubricating oils in machine installations so as to maintain performance. The lubricating oil temperature within tanks in machines and 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 admixture with moisture because of leaks from cooling water pipes.

**[0003]** US2006/090393 relates to the use of epoxidized esters as lubricant additives for imparting anticorrosion, anti-fatigue and anti-wear properties to the lubricant.

**[0004]** US-A-5275749 relates to lubricating oil compositions comprising N-acyl-N-hydrocarbonoxyalkyl aspartic acid esters which exhibit corrosion inhibition, anti-wear properties and improved demulsibility. WO 2008/031808 published on 20.03.2008 claiming the priority of 11.09.2006 discloses lubricating oil compositions comprising an aspartic acid derivative, an epoxidised fatty acid ester and a fatty acid ester of a polyhydric alcohol.

**[0005]** It is also necessary to inhibit as far as practicable the generation of sludge in the lubricating oils used in machine installations. If large quantities of sludge are generated because of deterioration under heat, for example, blockage of oil filter meshes may occur and sufficient supply of lubricating oil may not be possible, giving rise to breakdowns. Also, the sludge generated may accumulate in bearing parts and an adequate oil film may not form because of lacquer generated on bearing parts, giving rise to bearing damage. Further, in hydraulic installations, sludge may block the parts of the hydraulic circuit known as servo pumps, giving rise to breakdowns of the installation. Lubricating oil compositions with low sludge generation are therefore required.

**[0006]** Furthermore, in recent years good friction properties have been required of industrial lubricating oil compositions. This is because of the requirements of efficiently reducing friction losses in machines and apparatus and achieving large energy economies through having a low friction coefficient ($\mu$). Also, hydraulic apparatus is widely used in construction machines and so on, and if the friction coefficient of the lubricating oils 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 reciprocating packing 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. See Japanese Laid-open Patent 9-111277 (1997). In consequence it is necessary to reduce the friction coefficient of the lubricating oil so that the hydraulic cylinders move smoothly and accurately.

**[0007]** The present invention aims to obtain a lubricating oil composition having superior corrosion resistance properties as well as producing only small amounts of sludge. However, anti-corrosives added with a view to improving corrosion resistance may be substances giving rise to sludge, as a result of deterioration under heat. An important problem therefore is strike a balance between maintaining the anti-corrosive effect while inhibiting sludge.

**[0008]** Further important problems are to reduce the friction coefficients of lubricating oils and to obtain industrial lubricating oils having high energy savings. If a lubricating oil composition which resolves these problems is used for the hydraulic oils in hydraulic apparatus, the phenomena of chatter, vibration, squealing and other abnormal noises will not occur in the hydraulic cylinders and it will become possible to control the hydraulic apparatus with satisfactory precision. The present invention aims to obtain a lubricating oil composition which inhibits the generation of corrosion and sludge, which has abundant energy saving properties and which has good operational efficiency.

**[0009]** To this end the present invention provides a lubricating oil composition suitable as an industrial lubricating oil such as hydraulic oil by adding an aspartic acid derivative and an epoxidised ester compound as additives to a base oil, preferably being a highly refined base oil or a synthetic oil, having a sulphur content of not more than 300 ppm. Also, in a preferred embodiment, the present invention provides a lubricating oil composition with even less sludge generation and superior energy saving properties by further adding as an additive an aliphatic amine.

**[0010]** According to the present invention, it is possible to obtain a lubricating oil composition which inhibits the generation of corrosion and sludge. Further, it is possible to reduce effectively the friction losses caused in various kinds of industrial apparatus, and to ensure savings on energy. Also, if it is used as a hydraulic oil, it is possible, by reducing the friction coefficient, to control the hydraulic apparatus with satisfactory precision and without the occurrence of phenomena such as chatter, vibration, squealing or other abnormal noises in the hydraulic cylinders.

**[0011]** For the base oils of this lubricating oil composition it is possible to use the mineral oils and synthetic oils known as highly refined base oils. 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. For the base oils used here, the elemental sulphur content should be not more than 300 ppm, preferably not more than 200 ppm, more preferably not more than 100 ppm and most preferably not more than 50 ppm. Also, it is preferred that the density is from 0.8 to 0.9, preferably from 0.8 to 0.865, and more preferably from 0.81 to 0.83. The aromatic content is preferably less than 3%, more preferably less than 2% and even more preferably less than 0.1.

**[0012]** 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 the present invention. The viscosity of these base oils is not specially limited, but the viscosity index may be from 80 to 120 and preferably from 100 to 120. The kinetic viscosity at 40˚C (ASTM D445) is preferably from 2 to 680 $mm^2/s$ and even more preferably from 8 to 220 $mm^2/s$. Also, the total sulphur content may be less than 300 ppm, preferably less than 200 ppm and even more preferably less than 10 ppm. The total nitrogen content to be less than 10 ppm and preferably less than 1 ppm. In addition, oils with an aniline point of from 80 to 150˚C and preferably from 100 to 135˚C may be used.

**[0013]** Among Group III base oils and Group II+ base oils, 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 are suitable, for example. The viscosity of these base oils is not specially limited, but the viscosity index may be from 95 to 145 and preferably from 100 to 140. The kinetic viscosity at 40˚C may preferably be from 2 to 680 $mm^2/s$ and even more preferably from 8 to 220 $mm^2/s$. Also, the total sulphur content to be 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 of from 80 to 150˚C and preferably from 110 to 135˚C may be used.

**[0014]** GTLs (gas to liquid 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 the present invention. The viscosity characteristics of GTL base oils are not specially limited, but normally the viscosity index should be from 130 to 180 and preferably from 140 to 175. Also, the kinetic viscosity at 40˚C may be from 2 to 680 $mm^2/s$ and even more preferably from 5 to 120 $mm^2/s$. Normally, the total sulphur content may also be less than 10 ppm and the total nitrogen content may be less than 1 ppm. A commercial example of such a GTL derived base oil is Shell XHVI (registered trademark).

**[0015]** 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.

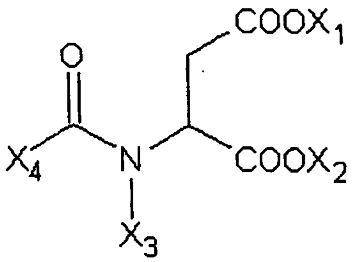
**[0016]** The above-mentioned polyolefins include polymers of various olefins or hydrides thereof. Any olefin may be used, and as examples mention may be made of ethylene, propylene, butene and α-olefins with five or more carbons. In the manufacture of polyolefins, one kind of the above-mentioned olefins 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.

**[0017]** The viscosity of these synthetic oils is not specially limited, but the kinetic viscosity at 40˚C may preferably be from 2 to 680 $mm^2/s$ and even more preferably from 8 to 220 $mm^2/s$.

**[0018]** The amount of the aforementioned base oil in the lubricating oil composition of the present invention is not specially limited, but on the basis of the total amount of the lubricating oil composition it is usually not less than 60 % by weight, preferably not less than 80 % by weight, more preferably not less than 90 % by weight and yet more preferably not less than 95 % by weight.

**[0019]** The aspartic acid derivatives are shown by the general formula 1.

Chemical structure 1



**[0020]** In the aforementioned general formula 1, $X_1$ and $X_2$ are each hydrogen atoms or same or different alkyl groups or hydroxyalkyl groups having from 3 to 6 carbon atoms, and for preference a 2-methylpropyl group and a tertiarybutyl group respectively are good. $X_3$ refers to alkyl groups constituted of from 1 to 30 carbon atoms, or alkyl groups having ether bonds, or hydroxyalkyl groups. For example, octadecyl groups, alkoxypropyl groups and 3-($C_6$-$C_{18}$) hydrocarbon oxy ($C_3$-$C_6$) alkyl groups are good, and preferably cyclohexyloxypropyl groups, 3-octyloxypropyl groups, 3-isooctyloxypropyl groups, 3-decyloxypropyl groups, 3-isodecyloxypropyl groups and 3-($C_{12}$-$C_{16}$) alkoxypropyl groups. $X_4$ refers to saturated or unsaturated carboxylic groups having from 1 to 30 carbon atoms, or alkyl groups having from 1 to 30 carbons, or alkenyl groups, or hydroxyalkyl groups. For example, propionic acid groups and propionyl acid groups are good.

**[0021]** The aforementioned aspartic acid derivative preferably has an acid number as determined by JIS K2501 of from 10 to 200 mgKOH/g, and preferably of from 50 to 150 mgKOH/g. The aspartic acid derivative is used in the lubricating agent composition in the order of from 0.01 to 5 % by weight and preferably in the order of from 0.05 to 2 % by weight.

**[0022]** The epoxidised ester compound may be manufactured by epoxidating 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. Mention may be made of epoxidised rapeseed oil esters, epoxidised soybean oil esters, epoxidised linseed oil esters, epoxidised castor oil esters, epoxidised safflower oil esters, and also of those manufactured by epoxidating oleic acid esters such as methyl epoxystearate, butyl epoxystearate and octyl epoxystearate.

**[0023]** Also, the alcohol residues of the esters may be alkyl groups, or alkyl groups having ether bonds, or hydroxyalkyl groups, and preferably butyl groups, isobutyl groups or 2-ethylhexyl groups.

**[0024]** As examples, mention may be made of epoxidised rapeseed fatty acid isobutyl ester, epoxidised rapeseed fatty acid 2-ethylhexyl ester and epoxidised linseed oil fatty acid butyl ester. The main constituents of ordinary rapeseed fatty acids are fatty acids of 18 carbons with oleic acid 63%, linolic acid 20% and linolenic acid 8%. The main constituents of linseed fatty acids are fatty acids of 18 carbons with oleic acid 21%, linolic acid 13% and linolenic acid 57%.

**[0025]** These epoxidised ester compounds are known as plasticisers and stabilisers in rubbers and plastics. The amount of epoxidised ester compound blended in the lubricating oil composition is from 0.01 to 5 per cent by weight, preferably from 0.01 to 2 per cent by weight, and even more preferably from 0.01 to 1 per cent by weight.

**[0026]** An aliphatic amine compound may further be incorporated in this lubricating oil composition, and as examples of such aliphatic amine compounds mention may be made of the primary amines shown in General Formula (2) and General Formula (3) and of the secondary amines show in General Formula (4).

Formula 2 $H_2N - X_5$ (2)

**[0027]** In the aforementioned formula (2), $X_5$ refers to saturated or unsaturated alkyl groups having from 1 to 30 carbon atoms. For example, 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. Preferably the number of carbons of $X_5$ is from 8 to 24 and more preferably from 12 to 18. Also, $X_5$ may be a tertiary alkyl group in either a straight-chain aliphatic or a branched-chain aliphatic.

Formula 3 $H_2N - X_6 - NH_2$ (3)

**[0028]** In the aforementioned formula (3), $X_6$ refers to saturated or unsaturated alkylene groups having from 1 to 30 carbon atoms. For example, mention may be made of ethylenediamines such as laurylethylenediamine, coconut ethylenediamine, n-tridecylethylenediamine, myristylethylenediamine, n-pentadecylethylenediamine, n-palmitylethylenediamine, n-heptadecylethylenediamine, n-stearylethylenediamine, isostearylethylenediamine, n-nonadecylethylenediamine, n-eicosylethylenediamine, n-heneicosylethylenediamine, n-docosylethylenediamine, n-tricosylethylenediamine, n-pentacosylethylenediamine, oleylethylenediamine, beef tallow ethylenediamine, hydrogenated beef tallow ethylenediamine and soybean ethylenediamine. Preferably the number of carbons of $X_6$ is from 8 to 24 and more preferably from 12 to 18.

Formula 4 $X_7 - NH - X_8$ (4)

**[0029]** In the aforementioned formula (4), $X_7$ and $X_8$ refer to saturated or unsaturated alkyl groups having from 1 to 30 carbon atoms. For example, mention may be made of dilaurylamine, di-coconut amine, di-n-tridecylamine, dinmyristylamine, 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. Preferably the number of carbons of $X_7$ and $X_8$ is from 8 to 24 and more preferably from 12 to 18. $X_7$ and $X_8$ may be the same or different.

**[0030]** At least one kind of these aliphatic amines selected from the aforementioned groups may be used in the lubricating agent composition in the order of approximately 0.005 to 5 % by weight, and preferably in the order of approximately 0.01 to 1 % by weight.

**[0031]** Apart from the aforementioned constituents, it is possible to make suitable use of various additives as necessary in order further to improve performance. 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, anticorrosion agents, demulsifiers, and other lubricating agents known in the art.

**[0032]** The anti-oxidants used in the present invention are preferably those used in practice in lubricating oils, 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 combinations within the range of 0.01 to 5 parts by weight relative to 100 parts by weight of the base oil.

**[0033]** As examples of the above mentioned amine-based anti-oxidants, mention may be made of dialkyl-diphenylamines such as p,p’-dioctyl-diphenylamine (Nonflex OD-3 manufactured by Seiko Kagaku 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 octylphenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine, aryl-naphthylamines such as 1-naphthylamine, 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 (manufactured by Hodogaya Chemical Co. Ltd.) and 3,7-dioctylphenothiazine.

**[0034]** As examples of sulphur-based anti-oxidants, mention may be made of dialkylsulphides such as didodecylsuplhide and dioctadecylsulphide, thiodipropionic acid esters such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and dodecyloctadecyl thiodipropionate, and 2-mercaptobenzimidazole.

**[0035]** The phenol-based 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, manufactured by Kawaguchi Kagaku 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.

**[0036]** They also include 3,5-di-t-butyl-4-hydroxybenzylmercapto-octyl acetate, 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, manufactured by Yoshitomi Pharmaceutical Industries Co. Ltd.), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 2’-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-C7-C9 branched alkyl esters (Irganox L135, manufactured by Ciba Speciality Chemicals Co. Ltd), 2,6-di-t-butyl-α-dimethylamino-p-cresol, and 2,2-methylenebis(4-alkyl-6-t-butylphenols) such as 2,2’-methylenebis(4-methyl-6-t-butylphenol) (Antage W-400, manufactured by Kawaguchi Kagaku Co. Ltd.) and 2,2’-methylenebis(4-ethyl-6-t-butylphenol) (Antage W-500, manufactured by Kawaguchi Kagaku Co. Ltd.).

**[0037]** They further include bisphenols such as 4,4’-butylidenebis(3-methyl-6-t-butylphenol) (Antage W-300, manufactured by Kawaguchi Kagaku Co. Ltd.), 4,4’-methylenebis(2,6-di-t-butylphenol) (Ionox 220AH, manufactured by Shell Japan Co. Ltd.), 4,4’-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A, manufactured by Shell Japan Co. Ltd.), 2,2-bis(3,5-dit-butyl-4-hydroxyphenyl)propane, 4,4-cyclohexylidenebis(2,6-t-butylphenol), hexamethylene glycolbis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] (Irganox L109, manufactured by Ciba Speciality Chemicals Co. Ltd), triethylene glycolbis[3-(3-t-qutyl-4-hydroxy-5-methylphenyl) propionate] (Tominox 917, manufactured by Yoshitomi Pharmaceutical Industries Co. Ltd.), 2,2’-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] (Irganox L115, manufactured by Ciba Speciality Chemicals Co. 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, manufactured by Sumitomo Chemicals Co. Ltd.), 4,4’-thiobis(3-methyl-6-t-butylphenol) (Antage RC, manufactured by Kawaguchi Kagaku Co. Ltd.) and 2,2’-thiobis(4,6-di-t-butylresorcinol).

**[0038]** Mention may also be made of tetrakis[methylene-3-3(3,5-di-t-butyl-4-hydroxyphenyl) propionate] methane (Irganox L101, manufactured by Ciba Speciality Chemicals Co. Ltd), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane (Yoshinox 930, manufactured by Yoshitomi Pharmaceutical Industries Co. Ltd.), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene (Ionox 330, manufactured by Shell Japan Co. Ltd.), bis-[3,3’-bis-(4’-hydroxy-3’-t-butylphenyl) butyric acid] glycol ester, polyphenols such as 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’-methylbenzyl)-4-methylphenol, and phenol-aldehyde condensates such as condensates of p-t-butylphenol and formaldehyde and condensates of p-t-butylphenol and acetaldehyde.

**[0039]** As examples of phosphorus-based anti-oxidants, mention may be made of triaryl phosphites such as triphenyl phosphite and tricresyl phosphite, trialkyl phosphites such as trioctadecyl phosphite and tridecyl phosphite, and tridodecyl trithiophosphite.

**[0040]** The metal deactivators which can be combined with the lubricating oil composition of the present invention include benzotriazole, benzotriazole derivatives of the 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, benzimidazole, and benzimidazole derivatives of the 2-(alkyldiothio)-benzimidazoles such as 2-(octyldithio)-benzimidazole, 2-(decyldithio)-benzimidazole and 2-(dodecyldithio)-benzimidazole and 2-(alkyldithio)-toluimidazoles such as 2-(octyldithio)-toluimidazole, 2-(decyldithio)-toluimidazole and 2-(dodecyldithio)- toluimidazole.

**[0041]** They also include indazole, indazole derivatives of the toluindazole derivatives such as 4-alkyl-indazoles and 5-alkyl-indazoles, benzothiazole, and benzothiazole derivatives of the 2-mercaptobenzothiazole derivatives (Thiolite B-3100, manufactured by Chiyoda Kagaku Co. Ltd.), 2-(alkyldithio)benzothiazoles such as (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-dihexyldithiocarbarnyl)-benzothiazole, 2-(N,N-dialkyldithiocarbarnyl)-toluthiazoles such as 2-(N,N-diethyldithiocarbamyl)toluthiazole, 2-(N,N-dibutyldithiocarbamyl)-toluthiazole and 2-(N,N-dihexyldithiocarbamyl)toluthiazole,

**[0042]** They further include benzoxazole derivatives of the 2-(alkyldithio)benzoxazoles such as 2-(octyldithio)-benzoxazole, 2-(decyldithio)benzoxazole and 2-(dodecyldithio)benzoxazole, and 2-(alkyldithio)toluoxazoles such as 2-(octyldithio)toluoxazole, 2-(decyldithio)toluoxazole and 2-(dodecyldithio)toluoxazole, thiadiazole derivatives of the 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, 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 of 1-alkyl-2,4-triazoles such as 1-di-octylaminomethyl-2,4-triazole. These metal deactivators may be used singly or in combinations within the range of 0.01 to 0.5 parts by weight relative to 100 parts by weight of the base oil.

**[0043]** In order to impart wear resistance and extreme pressure properties to the lubricating oil composition of the present invention it is possible also to add phosphorus compounds. As examples of compounds suitable for the present invention, mention may be made of phosphate esters, acidic phosphate esters, amine salts of acidic phosphate esters chlorinated phosphate esters, phosphite esters, phosphorothionates, zinc dithiophosphates, esters or derivatives thereof of dithiophosphates and alkanol or polyether-type alcohols, phosphorus-containing carboxylic acids, and phosphorus-containing organic carboxylate esters. These phosphorus compounds may be used singly or in combinations within the range of 0.01 to 2 parts by weight relative to 100 parts by weight of the base oil.

**[0044]** 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, triocyadecyl phosphate, trioleyl phosphate, triphenyl phosphate, tris(iso-propylphenyl) phosphate, triallyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyldiphenyl phosphate and xylenyldiphenyl phosphate.

**[0045]** 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, mononony 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.

**[0046]** As examples of the aforementioned amine salts of acidic phosphate esters, mention may be made of salts with amines of the of the above mentioned acidic phosphate esters such as methylamines, ethylamines, propylamines, butylamines, pentylamines, hexylamines, heptylamines, octylamines, dimethylamines, diethylamines, dipropylamines, dibutylamines, dipentylamines, dihexylamines, diheptylamines, dioctylamines, trimethylamines, triethylamines, tripropylamines, tributylamines, tripentylamines, trihexylamines, triheptylamines and trioctylamines.

**[0047]** 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, didodecyl 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.

**[0048]** As examples of the aforementioned phosphorothionates, mention may be made specifically of tributyl phosphorothionate, tripentyl phosphorothionate, 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 phosphorothionate, triphenyl phosphorothionate, tricresyl phosphorothionate, trixylenyl phosphorothionate, cresyldiphenyl phosphorothionate, xylenyldiphenyl phosphorothionate, tris(n-butylphenyl) phosphorothionate, tris(iso-butylphenyl) phosphorothionate, tris (s-butylphenyl) phosphorothionate and tris(t-butylphenyl) phosphorothionate. These may also be used in mixtures thereof.

**[0049]** 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, with respect to the alkyl groups of the zinc dialkyl dithiophosphates, zinc dialkyl dithiophosphates having 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 didodecyl dithiophosphate, zinc dipropylphenyl dithiophosphate, zinc dipentylphenyl dithiophosphate, zinc dipropylmethylphenyl dithiophosphate, zinc dinonylphenyl dithiophosphate, and zinc didodecylphenyl dithiophosphate.

**[0050]** Pour-point depressants and viscosity index improvers may also be added to the lubricating oil composition of the present invention in order to improve low-temperature flow characteristics and viscosity characteristics. As examples of viscosity index improvers, mention may be made of non-dispersant viscosity index improvers as exemplified by polymethacrylates and olefin polymers such as ethylene-propylene copolymers, styrene-diene copolymers, polyisobutylene and polystyrene, or dispersant-type viscosity index improvers which are copolymerised with nitrogen-containing monomers. The amount thereof added may be within the range of 0.05 to 20 parts by weight relative to 100 parts by weight of base oil.

**[0051]** As examples of pour-point depressants mention may be made of polymethacrylate based polymers. The amount thereof added may be within the range of 0.01 to 5 parts by weight relative to 100 parts by weight of base oil.

**[0052]** Defoaming agents may also be added in order to impart foaming resistance to the lubricating oil composition of the present invention. As examples of defoaming agents suitable for the present invention mention may be made of dimethylpolysiloxane, organosilicates such as diethylsilicate and fluorosilicones, and non-silicone defoaming agents such as polyalkylacrylates. The amount thereof added may be within the range of from 0.0001 to 0.1 part by weight relative to 100 parts by weight of base oil.

**[0053]** For demulsifiers suitable for the present invention mention may be made of those of the known art normally used as lubricating oil additives. The amount thereof added may be within the range of from 0.0005 to 0.5 part by weight relative to 100 parts by weight of base oil.

## Examples

**[0054]** The invention is explained in more detail below by means of Examples and Comparative Examples, but the invention is not limited to these Examples.

**[0055]** The following materials were used in preparing the Examples and Comparative Examples.

### 1. Base oils

**[0056]**

(1-1) Base Oil 1: A paraffinic mineral oil obtained by a suitable combination of refining procedures such as hydrocracking and dewaxing of a lubricating oil fraction obtained by atmospheric distillation of crude oil. Categorised as Group II (Gp II) according to the API (American Petroleum Institute) base oil categories.

(Characteristics: kinetic viscosity at 100˚C: 5.35 mm$^2$/s; kinetic viscosity at 40˚C: 31.4 mm$^2$/s; viscosity index: 103; density at 15˚C: 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 as determined by ASTM D3238: 62%; ditto naphthene content: 38%; ditto aromatic content: less than 1%; initial boiling point based on gas chromatography distillation as determined by ASTM D5480: 312˚C)

(1-2) Base Oil 2: A paraffinic mineral oil obtained by a suitable combination of refining procedures such as hydrocracking and dewaxing of a lubricating oil fraction obtained by atmospheric distillation of crude oil. Categorised as Group III (Gp III) according to the API (American Petroleum Institute) base oil categories.

(Characteristics: kinetic viscosity at 100˚C: 6.57 mm$^2$/s; kinetic viscosity at 40˚C: 37.5 mm$^2$/s; viscosity index: 130; density at 15˚C: 0.823; sulphur content (as converted to elemental sulphur): less than 10 ppm; nitrogen content (as converted to elemental nitrogen): less than 1 ppm; aniline point: 130˚C; ring-analysis paraffin content as determined by ASTM D3238: 78%; ditto naphthene content: 22%; ditto aromatic content: less than 1%; polycyclic aromatic content according to IP 346: 0.2%)

(1-3) Base Oil 3: A GTL oil synthesised by the Fischer-Tropsch method and categorised as Group III according to the API (American Petroleum Institute) base oil categories. (Characteristics: kinetic viscosity at 100˚C: 5.10 $mm^2/s$; kinetic viscosity at 40˚C: 23.5 $mm^2/s$; viscosity index: 153; density at 15˚C: 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 as determined by ASTM D3238: less than 1%)

(1-4) Base Oil 4: A poly-a-olefin synthetic oil, generally known as PAO6 and categorised as Group IV according to the API (American Petroleum Institute) base oil categories. (Characteristics: kinetic viscosity at 100˚C: 5.89 $mm^2/s$; kinetic viscosity at 40˚C: 31.2 $mm^2/s$; viscosity index: 135; density at 15˚C: 0.827; sulphur content (as converted to elemental sulphur): less than 10 ppm; nitrogen content (as converted to elemental nitrogen): less than 1 ppm; aniline point: 128˚C; ring-analysis aromatic content as determined by ASTM D3238: less than 1%; initial boiling point based on gas chromatography distillation as determined by ASTM D5480: 403˚C)

(1-5) Base Oil 5: A paraffinic mineral oil obtained by a suitable combination of refining procedures such as dewaxing of a lubricating oil fraction obtained by atmospheric distillation of crude oil. Categorised as Group I (Gp I) according to the API (American Petroleum Institute) base oil categories. (Characteristics: kinetic viscosity at 100˚C: 4.60 $mm^2/s$; kinetic viscosity at 40˚C: 24.6 $mm^2/s$; viscosity index: 101; density at 15˚C: 0.866; sulphur content (as converted to elemental sulphur): 460 ppm; nitrogen content (as converted to elemental nitrogen): 20 ppm; aniline point: 110˚C; ring-analysis paraffin content as determined by ASTM D3238: 66%; ditto naphthene content: 31%; ditto aromatics content: 3%; aniline point: 99˚C; polycyclic aromatic content according to IP 346: 0.8%; initial boiling point based on gas chromatography distillation as determined by ASTM D5480: 331˚C)

2. Additives

**[0057]**

(2-1) Additive A1: Aspartic acid derivative: K-CORR100, manufactured by King Co. Ltd., acid number according to the method of JIS K2501: 100 mgKOH/g

(2-2) Additive A2: Aspartic acid derivative: MONACOR 39, manufactured by Unichema Co. Ltd., acid number according to the method of JIS K2501: 60 mgKOH/g

(2-3) Additive B1: Epoxidised rapeseed fatty acid isobutyl ester

(2-4) Additive B2: Epoxidised rapeseed fatty acid 2-ethylhexyl ester

(2-5) Additive B3: Epoxidised linseed fatty acid butyl ester

(2-6) Additive B4: Epoxidised soybean oil

(2-7) Additive C1: Coconut amine (main constituent dodecylamine); primary amine compound of primary alkyl, base number according to the method of JIS K2501: 390 mgKOH/g.

(2-8) Additive C2: Oleylamine; primary alkyl primary amine compound, base number according to the method of JIS K2501: 215 mgKOH/g.

(2-9) Additive C3: Beef tallow amine (main constituents oleylamine, stearylamine, palmitylamine); primary alkyl primary amine compound, base number according to the method of JIS K2501: 215 mgKOH/g.

(2-10) Additive C4: Primary amine with C18 tertiary alkyl group; tertiary alkyl primary amine compound, base number according to the method of JIS K2501: 155 mgKOH/g.

(2-11)Additive C5: Coconut diamine (main constituent dodecyldiamine); primary alkyl primary diamine compound, base number according to the method of JIS K2501: 440 mgKOH/g.

(2-12) Additive C6: Coconut secondary amine (main constituent didodecylamine); primary alkyl secondary amine compound, base number according to the method of JIS K2501: 160 mgKOH/g.

(2-13) Other additives: The compounds shown below were mixed in: diphenylamine, phenylnaphthylamine, benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-$C_7$-$C_9$ branched alkyl ester, N,N-bis(2-ethylhexyl)-(4 or 5)-methyl-1H-benzotriazole-1-methylamine, triallyl phosphate, 3-(di-isobutoxythiophosphorylsulphanyl)-2-methylpropionic acid, pentaerythritol ester, polymethacrylate-type pour-point depressant, dimethylpolysiloxane-type defoaming agent, and polyoxyethylene·polyoxypropylene glycol-type demulsifier.

Examples 1 to 21, Comparative Examples 1 to 7

**[0058]** Using the aforementioned materials, the lubricating oil compositions of Examples 1 to 21 and Comparative Examples 1 to 7 were prepared in accordance with the compositions shown in Tables 1 to 7.

## Tests

**[0059]** Corrosion prevention tests and thermal stability tests were carried out as below on the lubricating oil compositions of Examples 1 to 21 and Comparative Examples 1 to 7 in order to see how they performed. Pendulum tests for friction coefficient were also carried out.

## Corrosion prevention test

**[0060]** In accordance with JIS K2510, 300 ml of the oil being tested was tapped off into a container disposed inside a constant temperature bath, and stirred at a speed of 1000 revolutions per minute. When the temperature reached 60˚C, an iron test-piece was inserted into the test oil, and 30 ml of artificial sea water was further added. The temperature was maintained at 60˚C while stirring continuously for 24 hours. The test-piece was then removed and assessed by eye for the presence of any rust. If no rust occurred, the oil was deemed to have passed.

## Thermal stability test

**[0061]** In accordance with Thermal Stability Test Procedure 'A' of Cincinnati Milacron Inc., 200 ml of the oil being tested was tapped off into a container disposed inside a constant temperature bath, and left there for 168 hours at 125˚C in the joint presence of a copper catalyst and an iron catalyst. Then, after cooling to room temperature, the sludge was gathered by a 5-micron filter and the amount of sludge generated was weighed. The figures in the tables are the amount of sludge per 200 ml of test oil (mg/200 ml).

**[0062]** The evaluation of the tests was made according to the following criteria:

| | |
|---|---|
| Amount of sludge generated less than 2.0 mg | Ø (Excellent) |
| Amount of sludge generated 2.0 to less than 10.0 mg | ○ (Good) |
| Amount of sludge generated 10.0 mg or more | X (Fail) |

## Pendulum test, friction coefficient

**[0063]** The friction coefficient at 25˚C was measured using a Masuda pendulum-type oiliness tester manufactured by Shinko Machine Manufacturing Co. Ltd. In this test the oil being tested is supplied to the friction portion of the pendulum fulcrum, the pendulum is made to move, and the friction coefficient is obtained from the reduction in oscillations.

**[0064]** The evaluation of the tests was made according to the following criteria:

| | |
|---|---|
| Friction coefficient 0.135 or less | Ø (Excellent) |
| Friction coefficient 0.136 to less than 150 | ○ (Good) |
| Friction coefficient 0.150 or more | X (Fail) |

## Test results

**[0065]** The results of the tests are shown in Tables 1 to 7.

## Discussion

**[0066]** As is clear from the results in Tables 1, 2 and 6, when the aspartic acid derivative of Comparative Example 2 (Additive A1) was added, it had adequate corrosion resistance but the amount of sludge generated in the thermal stability test was large. However, it was possible to reduce the amount of sludge while having adequate corrosion resistance by also using an epoxidised ester compound (Additive B1 or B2) as in Examples 1 to 3 and Example 8. Further, if the amount of epoxidised ester (Additive B1) incorporated was increased, the amount of sludge decreased and the sludge inhibition effect was more marked, as shown by Examples 1 to 3. Furthermore, as shown by Examples 1 to 6, the amount of sludge was small in lubricating oil compositions using any of the highly refined base oils 1 to 4, and in particular in the case of using the highly refined base oils shown in Examples 4 to 6, the amount of sludge was extremely small (Ø : excellent), and the sludge inhibition effect was even greater.

**[0067]** Similarly, as between Example 7 (Table 2) and Comparative Example 3 (Table 6), superior corrosion resistance and a superior sludge inhibition effect were obtained by using an aspartic acid derivative (Additive A2) together.with an epoxidised ester compound (Additive B1) in the base oil. Also, when looking at Example 9 (Table 2), the excellent corrosion resistance and excellent sludge inhibition effect of the aforementioned aspartic acid derivative and epoxidised ester compound were demonstrated even when using other additives with them.

**[0068]** In Examples 10 to 13 (Table 3), the sludge inhibition was even further improved by further using an aliphatic amine compound (Additive C1) in the base oil in addition to the aspartic acid derivative and epoxidised ester compound, and, given that the friction coefficient was considerably lower than in Comparative Examples 1 to 6 (Table 6), excellent low friction characteristics were demonstrated. In particular, when using Base Oil 3 (Example 12) and Base Oil 4 (Example 13), it was possible to make the friction coefficient considerably lower through the combination of these additives (Ø : excellent), and it was accordingly possible to impart excellent energy saving characteristics to the lubricating oil composition.

**[0069]** Also, in the case both of the aspartic acid derivative (Additive A2) used in Example 14 (Table 4) and of the epoxidised ester compound (Additive B2 or B3) used in Examples 15 to 16 (Table 4) excellent corrosion resistance, excellent sludge inhibition and excellent low friction characteristics were similarly obtained.

**[0070]** In the case of Examples 17 to 21 (Table 5), with various aliphatic amine compounds (Additives C2 to 6), excellent corrosion resistance, excellent sludge inhibition and excellent low friction characteristics were demonstrated through the combination of an aspartic acid derivative and epoxidised ester compound. In particular, a considerable sludge inhibition effect was obtained for Example of Embodiment 19 using an aliphatic amine compound (Additive C4). Also, in the case of Examples of Embodiment 17, 18 and 20 using aliphatic amine compounds (Additives C2, C3, C5), it was possible to reduce the friction coefficient considerably (Ø : excellent) and it was accordingly possible to impart excellent energy saving characteristics to the lubricating oil compositions.

**[0071]** It was evident, as shown by Comparative Example 6, that in the case of Base Oil 5, which had a high sulphur content, sludge inhibition was poor even when also using an aspartic acid derivative and an epoxidised ester compound. Also, as shown by Comparative Example 7, the sludge inhibition was poor also when there was an epoxy compound but with no esterisation.

Table 1

| | | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 |
|---|---|---|---|---|---|---|---|
| Composition | Base Oil 1: Gp II | 99.4 | 99.7 | 99.8 | | | |
| | Base Oil 2: GpIII | | | | 99.4 | | |
| | Base Oil 3: GTL | | | | | 99.4 | |
| | Base Oil 4: PAO | | | | | | 99.4 |
| | Additive A1: Aspartic acid derivative K-CORR 100 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| | Additive B1: Epoxidised ester compound | 0.5 | 0.2 | 0.1 | 0.5 | 0.5 | 0.5 |
| Test results | Corrosion prevention test | Pass | Pass | Pass | Pass | Pass | Pass |
| | Thermal stability test Sludge generated (mg/200 ml) | O<br>3.6 | O<br>5.1 | O<br>8.5 | Ø<br>1.0 | Ø<br>0.4 | Ø<br>1.0 |

Table 2

| | | Example 7 | Example 8 | Example 9 |
|---|---|---|---|---|
| Composition | Base Oil 1: GpII | 99.4 | 99.4 | |
| | Base Oil 3: GTL | | | 98.9 |
| | Additive A1: Aspartic acid derivative K-CORR 100 | | 0.1 | 0.1 |
| | Additive A2: Aspartic acid derivative MONACOR 39 | 0.1 | | |
| | Additive B1: Epoxidised ester compound | 0.5 | | 0.5 |
| | Additive B2: Epoxidised ester compound | | 0.5 | |
| | Other additives | | | 0.5 |
| Test results | Corrosion prevention test | Pass | Pass | Pass |
| | Thermal stability test<br>Sludge generated (mg/200 ml) | ○<br>6.4 | ○<br>3.4 | ○<br>3.7 |

Table 3

| | | Example 10 | Example 11 | Example 12 | Example 13 |
|---|---|---|---|---|---|
| Composition | Base Oil 1: Gp II | 99.2 | | | |
| | Base Oil 2: GpIII | | 99.2 | | |
| | Base Oil 3: GTL | | | 99.2 | |
| | Base Oil 4: PAO | | | | 99.2 |
| | Additive A1: Aspartic acid derivative K-CORR 100 | 0.1 | 0.1 | 0.1 | 0.1 |
| | Additive B1: Epoxidised ester compound | 0.5 | 0.5 | 0.5 | 0.5 |
| | Additive C1: Coconut amine | 0.2 | 0.2 | 0.2 | 0.2 |
| Test results | Corrosion prevention test | Pass | Pass | Pass | Pass |
| | Thermal stability test Sludge generated (mg/200 ml) | Ø<br>1.4 | Ø<br>0.1 | Ø<br>0.3 | Ø<br>0.9 |
| | Pendulum test Friction coefficient | O<br>0.146 | O<br>0.138 | Ø<br>0.120 | Ø<br>0.133 |

Table 4

| | | Example 14 | Example 15 | Example 16 |
|---|---|---|---|---|
| Composition | Base Oil 1: GpII | 99.2 | 99.2 | 99.2 |
| | Additive A1:<br>Aspartic acid derivative K-CORR 100 | | 0.1 | 0.1 |
| | Additive A2:<br>Aspartic acid derivative MONACOR 30 | 0.1 | | |
| | Additive B1:<br>Epoxidised ester compound | 0.5 | | |
| | Additive B2:<br>Epoxidised ester compound | | 0.5 | |
| | Additive B3:<br>Epoxidised ester compound | | | 0.5 |
| | Additive C1:<br>Coconut amine | 0.2 | 0.2 | 0.2 |
| Test results | Corrosion prevention test | Pass | Pass | Pass |
| | Thermal stability test<br>Sludge generated (mg/200 ml) | Ø<br>1.5 | Ø<br>0.8 | O<br>2.5 |
| | Pendulum test<br>Friction coefficient | O<br>0.138 | O<br>0.140 | Ø<br>0.135 |

Table 5

| | | Example 17 | Example 18 | Example 19 | Example 20 | Example 21 |
|---|---|---|---|---|---|---|
| Composition | Base Oil 1: Gp II | 99.2 | 99.2 | 99.2 | 99.2 | 99.2 |
| | Additive A1: Aspartic acid derivative K-CORR 100 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| | Additive B1: Epoxidised ester compound | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | Additive C2: Oleylamine | 0.2 | | | | |
| | Additive C3: Beef tallow amine | | 0.2 | | | |
| | Additive C4: C18 tertiary alkyl primary amine compound | | | 0.2 | | |
| | Additive C5: Coconut amine | | | | 0.2 | |
| | Additive C6: Coconut secondary amine | | | | | 0.2 |
| Test results | Corrosion prevention test | Pass | Pass | Pass | Pass | Pass |
| | Thermal stability test<br>Sludge generated (mg/200 ml) | O<br>5.4 | O<br>4.5 | Ø<br>1.9 | O<br>7.8 | O<br>4.5 |
| | Pendulum test<br>Friction coefficient | Ø<br>0.134 | Ø<br>0.133 | O<br>0.144 | Ø<br>0.115 | O<br>0.139 |

Table 6

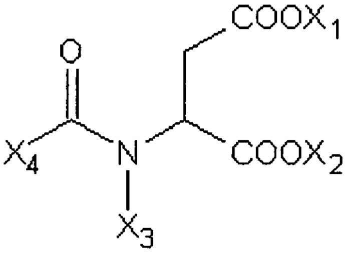
| | | Comp. Ex. 1 | Comp. Ex. 2 | Comp. Ex. 3 | Comp. Ex. 4 | Comp. Ex. 5 |
|---|---|---|---|---|---|---|
| Composition | Base Oil 1: Gp II | 100.0 | 99.9 | 99.9 | 99.5 | 99.8 |
| | Additive A1:<br>Aspartic acid derivative<br>K-CORR 100 | | 0.1 | | | |
| | Additive A2:<br>Aspartic acid derivative<br>MONACOR 39 | | | 0.1 | | |
| | Additive B1:<br>Epoxidised ester compound | | | | 0.5 | |
| | Additive C1:<br>Coconut amine | | | | | 0.2 |
| Test results | Corrosion prevention test | Fail | Pass | Pass | Fail | Fail |
| | Thermal stability test<br>Sludge generated (mg/200 ml) | Ø<br>0.6 | X<br>16.3 | X<br>34.6 | Ø<br>0.8 | Ø<br>0.8 |
| | Pendulum test<br>Friction coefficient | X<br>0.307 | X<br>0.167 | X<br>0.181 | X<br>0.294 | X<br>0.193 |

Table 7

| | | Comp. Ex. 6 | Comp. Ex. 7 |
|---|---|---|---|
| Composition | Base Oil 1: Gp II | | 99.4 |
| | Base Oil 5: Gp I | 99.4 | |
| | Additive A1: Aspartic acid derivative K-CORR 100 | 0.1 | 0.1 |
| | Additive B1: Epoxidised ester compound | 0.5 | |
| | Additive B4: Epoxy compound | | 0.5 |
| Test results | Corrosion prevention test | Pass | Pass |
| | Thermal stability test<br>Sludge generated (mg/200 ml) | X<br>47.7 | X<br>116.3 |

## Claims

1. Lubricating oil composition comprising a base oil having a sulphur content of not more than 300 ppm, an aspartic acid derivative, and an epoxidised ester compound,
   wherein the aspartic acid derivative has general formula 1



wherein $X_1$ and $X_2$ are each hydrogen atoms or same or different alkyl groups or hydroxyalkyl groups having from 3 to 6 carbon atoms;
$X_3$ is an alkyl group having 1 to 30 carbon atoms, possibly containing an ether bond and/or a hydroxyalkyl group;
$X_4$ is an $C_1$ - $C_{30}$ saturated or unsaturated carboxylic group, alkyl group, an ethylhexyl group or hydroxyalkyl group, wherein the amount of each of the aspartic acid derivative and epoxidised ester compound is from 0.01 to 5 % by weight, based on the total composition,
and wherein is excluded a lubricating oil composition comprising a base oil and as additives an aspartic acid derivative having formula I above and a fatty acid ester of a polyhydric alcohol, further comprising an epoxy compound which is an epoxidised fatty acid ester derived from an animal oil or fat or vegetable oil or fat-.

2. Lubricating oil composition according to Claim 1, wherein the acid number of the aspartic acid derivative is from 10 to 250 mgKOH/g.

3. Lubricating oil composition according to Claim 1 or 2, wherein the epoxidised ester compound is an epoxidised fatty acid ester derived from animal oils and fats and/or vegetable oils and fats.

**4.** Lubricating oil composition according to any of Claims 1 to 3 further comprising an aliphatic amine.

**5.** Lubricating oil composition according to Claim 4 wherein the amount of aliphatic amine is from 0.005 to 5% by weight, based on the total composition.

**6.** Lubricating oil composition according to Claim 4 or 5, wherein the aliphatic moiety of the fatty acid amine has from 8 to 24 carbons.

**7.** Lubricating oil composition according to any of Claims 1 to 6, wherein the base oil is a synthetic oil.

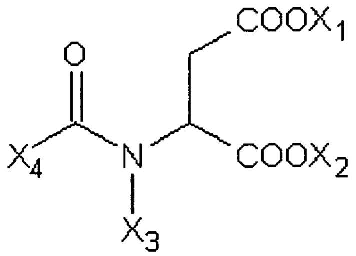
**8.** Lubricating oil composition according to Claim 7, wherein the base oil is a poly-α-olefin.

**9.** Lubricating oil composition according to Claim 7, wherein the base oil is a GTL derived base oil.

**10.** Use of the lubricating oil composition according to any of the Claims 1 to 9 as a machine oil, hydraulic oil, turbine oil, compressor oil, gear oil, sliding friction oil, bearing oil and calibration oil.

**11.** Method of improving the lubrication by using the lubricating oil composition according to one or more of the preceding Claims 1 to 9.

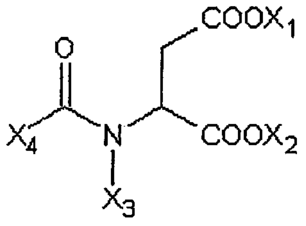
**12.** Use of a lubricating oil composition comprising a base oil having a sulphur content of not more than 300 ppm, an aspartic acid derivative, and an epoxidised ester compound,
wherein the aspartic acid derivative has general formula 1



wherein $X_1$ and $X_2$ are each hydrogen atoms or same or different alkyl groups or hydroxyalkyl groups having from 3 to 6 carbon atoms;
$X_3$ is an alkyl group having 1 to 30 carbon atoms, possibly containing an ether bond and/or a hydroxyalkyl group;
$X_4$ is an $C_1$ - $C_{30}$ saturated or unsaturated carboxylic group, alkyl group, an ethylhexyl group or hydroxyalkyl group, and wherein the amount of each of the aspartic acid derivative and epoxidised ester compound is from 0.01 to 5 % by weight, based on the total composition,
for inhibiting the generation of sludge.

## Patentansprüche

**1.** Schmierölzusammensetzung, umfassend ein Basisöl mit einem Schwefelgehalt von nicht mehr als 300 pp, ein Asparaginsäurederivat und eine epoxidierte Esterverbindung,
wobei das Asparaginsäurederivat die allgemeine Formel 1 aufweist:



wobei $X_1$ und $X_2$ jeweils Wasserstoffatome oder gleiche oder unterschiedliche Alkylgruppen oder Hydroxyalkylgruppen, die 3 bis 6 Kohlenstoffatome aufweisen, sind,
$X_3$ eine Alkylgruppe ist, die 1 bis 30 Kohlenstoffatome aufweist, und die möglicherweise eine Etherbindung und/oder eine Hydroxyalkylgruppe enthält,
$X_4$ eine gesättigte oder ungesättigte $C_1$-$C_{30}$-Carboxylgruppe, Alkylgruppe, eine Ethylhexylgruppe oder Hydroxyalkylgruppe ist,
wobei die Menge jedes Asparaginsäurederivats und der epoxidierten Esterverbindung zwischen 0,01 bis 5 Gew.-% bezogen auf die gesamte Zusammensetzung beträgt,
und wobei eine Schmierölzusammensetzung ausgeschlossen ist, die ein Basisöl und als Zusatzstoffe ein Asparaginsäurederivat der vorstehenden Formel 1 und einen Fettsäureester von einem mehrwertigen Alkohol enthält, ferner umfassend eine Epoxyverbindung, bei der es sich um einen epoxidierten Fettsäureester handelt, der aus einem tierischen Öl oder Fett oder einem planzlichen Öl oder Fett gewonnen wurde.

2. Schmierölzusammensetzung nach Anspruch 1, wobei die Säurezahl des Asparaginsäurederivats zwischen 10 bis 250 mgKOH/g liegt.

3. Schmierölzusammensetzung nach Anspruch 1 oder 2, wobei die epoxidierte Esterverbindung ein epoxidierter Fettsäureester ist, der aus tierischen Ölen bzw. Fetten und/oder pflanzlichen Ölen bzw. Fetten gewonnen wurde.

4. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 3, ferner umfassend ein aliphatisches Amin.

5. Schmierölzusammensetzung nach Anspruch 4, wobei die Menge des aliphatischen Amins zwischen 0,005 bis 5 Gew.-% bezogen auf die gesamte Zusammensetzung beträgt.

6. Schmierölzusammensetzung nach Anspruch 4 oder 5, wobei der aliphatische Rest des Fettsäureamins 8 bis 24 Kohlenstoffe aufweist.

7. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, wobei das Basisöl ein syntetisches Öl ist.

8. Schmierölzusammensetzung nach Anspruch 7, wobei das Basisöl ein Poly-$\alpha$-Olefin ist.

9. Schmierölzusammensetzung nach Anspruch 7, wobei das Basisöl ein im GtL-Verfahren (Gas to Liquids) gewonnenes Basisöl ist.

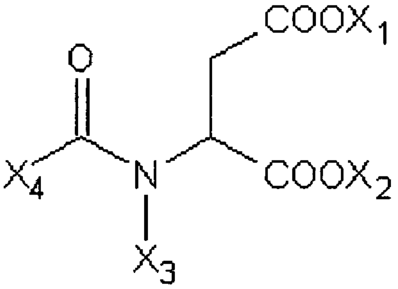
10. Verwendung der Schmierölzusammensetzung nach einem der Ansprüche 1 bis 9 als Maschinenöl, Hydrauliköl, Turbinenöl, Kompressoröl, Getriebeöl, Gleitreibungsöl, Lageröl und Kalibrieröl.

11. Verfahren zur Verbesserung der Schmierfähigkeit durch Verwendung der Schmierölzusammensetzung nach einem oder mehreren der vorangehenden Ansprüche 1 bis 9.

12. Verwendung einer Schmierölzusammensetzung, umfassend ein Basisöl, mit einem Schwefelgehalt von nicht mehr als 300 ppm, ein Asparaginsäurederivat und eine epoxidierte Esterverbindung, wobei das Asparaginsäurederivat die folgende allgemeine Formel 1 aufweist:
wobei $X_1$ und $X_2$ jeweils Wasserstoffatome oder gleiche oder unterschiedliche Alkylgruppen oder Hydroxyalkylgruppen sind, die zwischen 3 bis 6 Kohlenstoffatome aufweisen,
$X_3$ eine Alkylgruppe ist, die 1 bis 30 Kohlenstoffatome aufweist, und die möglicherweise eine Etherbindung und/oder eine Hydroxyalkylgruppe enthält,
$X_4$ eine gesättigte oder ungesättigte $C_1$-$C_{30}$-Carboxylgruppe, Alkylgruppe, eine Ethylhexylgruppe oder Hydroxyalkylgruppe ist,
und wobei die Menge jedes Asparaginsäurederivats und der epoxidierten Esterverbindung zwischen 0,01 bis 5 Gew.-% bezogen auf die gesamte Zusammensetzung beträgt, um Schlackebildung zu verhindern.

## Revendications

1. Composition d’huile lubrifiante comprenant une huile de base ayant une teneur en soufre de pas plus de 300 ppm, un dérivé d’acide aspartique et un composé d’ester époxydé,
dans laquelle le dérivé d’acide aspartique a la formule générale I :



dans laquelle $X_1$ et $X_2$ sont chacun des atomes d'hydrogène ou des groupements alkyle ou hydroxyalkyle identiques ou différents de 3 à 6 atomes de carbone ;
$X_3$ est un groupement alkyle ayant 1 à 30 atomes de carbone, contenant éventuellement une liaison éther et/ou un groupement hydroxyalkyle ;
$X_4$ est un groupement carboxylique saturé ou insaturé en $C_1$-$C_{30}$, un groupement alkyle, un groupement éthylhexyle ou un groupement hydroxyalkyle,
dans laquelle la quantité de chacun du dérivé d'acide aspartique et du composé d'ester époxydé est de 0,01 à 5 % en poids, sur la base de la composition totale, et
dans laquelle est exclue une composition d'huile lubrifiante comprenant une huile de base et, comme additifs, un dérivé d'acide aspartique ayant la formule I ci-dessus et un ester d'acide gras d'un alcool polyvalent, comprenant en outre un composé époxydé qui est un ester d'acide gras époxydé dérivé d'une huile ou d'une graisse animale ou d'une huile ou d'une graisse végétale.

**2.** Composition d'huile lubrifiante selon la revendication 1, dans laquelle l'indice d'acide du dérivé d'acide aspartique est de 10 à 250 mg de KOH/g.

**3.** Composition d'huile lubrifiante selon la revendication 1 ou la revendication 2, dans laquelle le composé d'ester époxydé est un ester d'acide gras époxydé dérivé d'huiles et de graisses animales et/ou d'huiles et de graisses végétales.

**4.** Composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 3, comprenant en outre une amine aliphatique.

**5.** Composition d'huile lubrifiante selon la revendication 4, dans laquelle la quantité d'amine aliphatique est de 0,005 à 5 % en poids, sur la base de la composition totale.

**6.** Composition d'huile lubrifiante selon la revendication 4 ou la revendication 5, dans laquelle le radical aliphatique de l'amine d'acide gras a 8 à 24 atomes de carbone.

**7.** Composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 6, dans laquelle l'huile de base est une huile synthétique.

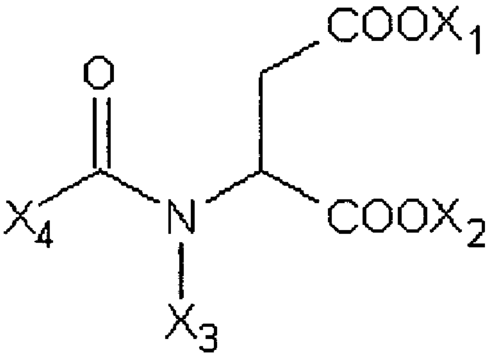
**8.** Composition d'huile lubrifiante selon la revendication 7, dans laquelle l'huile de base est une poly-$\alpha$-oléfine.

**9.** Composition d'huile lubrifiante selon la revendication 7, dans laquelle l'huile de base est une huile de base dérivée de GTL.

**10.** Utilisation de la composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 9 comme huile de machine, huile hydraulique, huile de turbine, huile de compresseur, huile d'engrenage, huile de friction de pièces coulissantes, huile de palier et huile de calibrage.

**11.** Procédé d'amélioration de la lubrification en utilisant la composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 9.

**12.** Utilisation d'une composition d'huile lubrifiante comprenant une huile de base ayant une teneur en soufre de pas plus de 300 ppm, un dérivé d'acide aspartique et un composé d'ester époxydé,
dans laquelle le dérivé d'acide aspartique a la formule générale I :



dans laquelle $X_1$ et $X_2$ sont chacun des atomes d'hydrogène ou des groupements alkyle ou hydroxyalkyle identiques ou différents de 3 à 6 atomes de carbone ;
$X_3$ est un groupement alkyle ayant 1 à 30 atomes de carbone, contenant éventuellement une liaison éther et/ou un groupement hydroxyalkyle ;
$X_4$ est un groupement carboxylique saturé ou insaturé en $C_1$-$C_{30}$, un groupement alkyle, un groupement éthylhexyle ou un groupement hydroxyalkyle, et
dans laquelle la quantité de chacun du dérivé d'acide aspartique et du composé d'ester époxydé est de 0,01 à 5 % en poids, sur la base de la composition totale, pour inhiber la génération de boue.

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- US 2006090393 A **[0003]**
- US 5275749 A **[0004]**
- WO 2008031808 A **[0004]**
- JP 9111277 A **[0006]**