

(19) AUSTRALIAN PATENT OFFICE

(54) Title
Lubricating oil composition

(51) ⁶ International Patent Classification(s)
C10M 169/04 060101BHAU
(2006.01) PCT/EP02/0004
C10M 169/04 1
20060101AFI20

(21) Application No: 2002224973 (22) Application Date: 2002.01.02

(87) WIPO No: W002/053687

(30) Priority Data

(31) Number	(32) Date	(33) Country
2001-93	2001.01.04	JP
2001-57423	2001.03.01	JP

(43) Publication Date : 2002.07.16

(43) Publication Journal Date : 2003.01.23

(71) Applicant(s)
Shell Internationale Research Maatschappij B.V.

(72) Inventor(s)
Baba, Yoshiharu

(74) Agent/Attorney
Spruson & Ferguson, Level 35 St Martins Tower 31 Market
Street, Sydney, NSW, 2000

(56) Related Art
US 5362419 A
WO 2000/011122 A
US 5922657 A
GB1347845 A

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 July 2002 (11.07.2002)

PCT

(10) International Publication Number
WO 02/053687 A3

- (51) International Patent Classification: C10M 169/04 // 137:10, 137:04, C10N 40:04, 40:08, 30:06
- (21) International Application Number: PCT/EP02/00041
- (22) International Filing Date: 2 January 2002 (02.01.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2001-93 4 January 2001 (04.01.2001) JP
2001-57423 1 March 2001 (01.03.2001) JP
- (71) Applicant (for all designated States except US): SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): BABA, Yoshiharu [JP/JP]; 4052-2 Nakatsu, Aikawa-cho, Aiko-gun, Kanagawa 243 0303 (JP).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GI, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report:
19 September 2002
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/053687 A3

(54) Title: LUBRICATING OIL COMPOSITION

(57) Abstract: Lubricating oil composition comprising β -dithiophosphorylated propionic acid (A), triaryl phosphate (B) and base oil comprising mineral oil and/or synthetic oil.

LUBRICATING OIL COMPOSITION

The present invention relates to a lubricating oil composition which exhibits excellent lubricating performance, even under severe high pressure/high load working conditions.

5 The use of industrial machines at higher speeds, under higher pressures, and the miniaturization thereof has resulted in machine elements such as hydraulic machines, compressors, turbines, gear elements and bearings being operated under severer conditions.

10 The lubricating oil used must therefore exhibit excellent lubricating performance to sufficiently guarantee the life of these machines over long periods even when they are used at high pressure, high speed, high load and high temperatures.

15 In response to these demands, zinc dialkyl dithiophosphates have been used in anti-wear lubricating oil compositions for lubricating oils for industrial machines. However these compounds are disadvantageous in terms of their instability to hydrolysis on contamination with water and their instability to thermal oxidation at
20 high temperature and high pressure, and in that an unpleasant odour is generated as the lubricating oil deteriorates.

 In addition to the abovementioned problems, there
25 are increasing concerns over the use of zinc compounds such as zinc dialkyl dithiophosphates in view of recent questions regarding environmental protection and toxicity.

 Anti-wear lubricating oil compositions comprising
30 sulphur compounds, phosphorous compounds and phosphorous-sulphur-based combinations thereof are already known as

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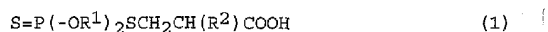
zinc-free anti-wear lubricating oils which do not contain zinc dialkyl dithiophosphates.

Specifically, the combination of sulphurated hydrocarbon and acidic phosphoric acid ester and the
5 combination of triaryl phosphorothionate, triaryl phosphate and acidic phosphate ester amine salt, as disclosed in GB Patent Number 1415964, are known, but the corrosive properties and odour of sulphurated hydrocarbon poses problems, and highly active acidic phosphate esters
10 are disadvantageous in that, for example, they cause hydrolytic deterioration and a decrease in thermal oxidation stability.

The present invention therefore aims to provide a lubricating oil composition which contains as little ash
15 (e.g. zinc) as possible and has excellent anti-wear properties, even when used under severe high pressure, high speed and high load conditions, and which is excellent in terms of its thermal oxidation stability, water resistance and odour and also in terms of the
20 environment, safety and its lubricating oil performance in practice.

The present invention provides a lubricating oil composition, comprising β -dithiophosphorylated propionic acid (A), triaryl phosphate (B) and base oil comprising
25 mineral oil and/or synthetic oil.

In a preferred embodiment, β -dithiophosphorylated propionic acid (A) is represented by the general formula (1) below:-



30 wherein R^1 , which may be identical or different, represents a branched alkyl group of from 3 to 8 carbon atoms, preferably from 3 to 4 carbon atoms, and R^2 represents a hydrogen atom or an alkyl group of from 1 to 4 carbon atoms.

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R¹ can be chosen from the following branched alkyl groups:- isopropyl group, branched butyl group, branched pentyl group, branched hexyl group, branched heptyl group, and branched octyl group.

5 Examples of R² include hydrogen, methyl, ethyl, propyl and butyl groups. Preferably, R² is a methyl group, ethyl group or hydrogen group. It is particularly preferred that R² is methyl.

Specific examples of such compounds include
10 3-(O,O-diisopropyldithiophosphoryl)propionic acid,
3-(O,O-diisopropyldithiophosphoryl)-2-methyl-propionic acid, 3-(O,O-diisobutyldithiophosphoryl)-propionic acid and 3-(O,O-diisobutyldithiophosphoryl)-2-methyl-propionic acid.

15 The amount of β-dithiophosphorylated propionic acid (A) added in the present invention is preferably from 0.001 to 1.0 % by weight, more preferably from 0.001 to 0.5 % by weight, even more preferably from 0.001 to 0.1 % by weight, and most preferably from 0.005 to 0.05 % by
20 weight, with respect to the total amount of lubricating oil composition.

If the amount of (A) added is less than 0.001 % by weight, adequate synergistic effects may not be achieved, whereas if the amount of (A) added exceeds 0.5 % by
25 weight, the lubricating performance reaches saturation, and there may be a deterioration in thermal oxidation stability, hydrolysis stability and corrosion properties, which is undesirable.

In a preferred embodiment, the triaryl phosphate (B) is represented by the general formula (2) below:-
30



wherein each R³ is independently a phenyl group or a phenyl group having alkyl group(s) of from 1 to 9 carbon atoms.

Specific examples of suitable triaryl phosphates (B) include triphenyl phosphate ester, tricresyl phosphate ester, triethyl phenyl phosphate ester, tripropyl phenyl phosphate ester, tributyl phenyl phosphate ester, triheptyl phenyl phosphate ester, trihexyl phenyl phosphate ester, triheptyl phenyl phosphate ester, trioctyl phenyl phosphate ester and trinonyl phenyl phosphate ester.

The amount of triaryl phosphate (B) used in the present invention is preferably from 0.05 to 10 % by weight, more preferably from 0.05 to 5 % weight and most preferably from 0.1 to 2 % by weight with respect to the total amount of lubricating oil base oil.

If less than 0.05 % by weight of (B) is added, sufficient lubricating performance may not be achieved, whereas if more than 10 % by weight of (B) is added, the lubricating performance reaches saturation and there may be a deterioration in thermal oxidation stability and hydrolysis stability, which is undesirable.

In a preferred embodiment of the present invention, the lubricating oil composition exhibits wear corresponding to no more than 150 mg, which meets DIN 51524 (Part 2) standard, in a "Vickers V104 C" vane pump test (according to IP 281).

In another preferred embodiment of the present invention, the lubricating oil composition exhibits vane wear corresponding to no more than 15 mg and ring wear corresponding to no more than 75 mg, which meets "Vickers" standard M-2950-S, in a "Vickers 35VQ25A" vane pump test (according to "Vickers" M-2950-S).

In yet another preferred embodiment of the present invention, the lubricating oil composition exhibits vane wear corresponding to no more than 10 mg and ring wear corresponding to no more than 50 mg, which meets "General

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Motors" Standard LS-2LH.03.04.06, in a "Vickers 35VQ25A" vane pump test (according to "Vickers" M-2950-S).

The lubricating oil composition according to the present invention may be used as a hydraulic oil
5 composition, a compressor oil composition, a turbine oil composition, a bearing oil composition, and/or a gear oil composition.

There are no particular limitations regarding the base oil in the lubricating oil composition of the
10 present invention. Preferably, said base oil is petroleum-based, synthetic hydrocarbon-based and/or ester-based.

The preferred physical properties of the base oil are as follows:

15 a kinematic viscosity of from 2 to 680 mm²/s (40°C), preferably from 5 to 320 mm²/s (40°C) and more preferably from 8 to 220 mm²/s (40°C);

a total sulphur content (% by weight) of from 0 to 1% and preferably from 0 to 0.3%;

20 a total nitrogen content (weight ppm) of from 0 to 100 ppm and preferably from 0 to 30 ppm; and/or

an aniline point of from 80 to 130°C and preferably from 100 to 125°C.

Petroleum-based lubricating oil base oils which can
25 be used in the present invention include solvent purified base oil, hydrogenation purified base oil and highly hydrocracked base oil. Such base oils can be used individually or as mixtures.

Highly hydrocracked base oil is a base oil having a
30 viscosity index of at least 130 (typically from 145 to 155). Said base oil can be obtained by taking a starting material wax (slack wax) which has been separated by solvent dewaxing, and hydrogenating said wax in the presence of a catalyst (catalytic degradation) to convert
35 linear paraffin to branched paraffin. Alternatively,

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said base oil can be obtained by taking as starting material the hydrogen and carbon monoxide obtained by subjecting natural gas (methane or the like) to the gas formation process (partial oxidation), then subjecting
5 said starting material to Fischer-Tropsch polymerisation to yield heavy linear paraffin, and then modifying said heavy linear paraffin to catalytic degradation as described above.

The synthetic hydrocarbon-based base oil used in the
10 present invention can be an olefin oligomer obtained by homopolymerizing or copolymerizing monomer chosen from linear or branched olefinic hydrocarbons of from 3 to 15, preferably from 4 to 12, carbon atoms.

In the present invention, petroleum-based base oil
15 or synthetic hydrocarbon-based base oil can be used individually, or in mixtures thereof.

Triaryl phosphate esters have long been known as anti-wear agents for use under relatively mild conditions, and, as disclosed in US Patent Number 5922657
20 (corresponding to Japanese Unexamined Patent Application Number H10-67993), β -dithiophosphorylated propionic acid is known to improve extreme pressure performance and prevent gear seizure.

However, in the present invention, the anti-wear
25 properties under severe high pressure/high load conditions can be improved to equivalent to or better than those achieved when β -dithiophosphorylated propionic acid is used alone, by the combined use of the abovementioned anti-wear component triarylphosphate
30 ester.

In addition to the abovementioned indispensable components, various other commonly used additives may also be added if necessary in the present invention in order to further improve performance.

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Thus, it is possible to add commonly known lubricating oil additives such as antioxidant, rust preventer, metal deactivator, detergent dispersant, anti-wear agent, extreme-pressure agent, friction regulator, flow point depressor, viscosity index improver, anti-emulsification agent and defoamer.

For example, examples of amine-based antioxidants include dialkyldiphenylamines such as p,p'-dioctyldiphenylamine (manufactured by Seiko Kagaku under the trade designation "Nonflex OD-3"), p,p'-di- α -methylbenzyldiphenylamine and N-p-butylphenyl-N'-octylphenylamine; monoalkyldiphenylamines such as mono-t-butylphenylamine and mono-octyldiphenylamines; 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 Kagaku: Phenothiazine) and 3,7-dioctylphenothiazine.

Examples of sulphur-based antioxidants include dialkyl sulphates such as didodecyl sulphate and dioctadecyl sulphate, thiodipropionic acid esters such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and dodecyloctadecyl thiodipropionate, and 2-mercaptobenzimidazole.

Examples of phenol-based antioxidants include 2,6-di-t-butyl-4-alkylphenols such as 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-

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butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone (manufactured by Kawaguchi Kagaku under the trade designation "Antage DBH"), 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol; 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol; alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionates such as 3,5-di-t-butyl-4-hydroxybenzylmercaptooctyl acetate, n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate (manufactured by Yoshitomi Seiyaku under the trade designation "Yoshinox SS"), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate; 2,6-di-t-butyl- α -dimethylamino-p-cresol; 2,2'-methylenebis(4-alkyl-6-t-butylphenol)s such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (manufactured by Kawaguchi Kagaku under the trade designation "Antage W-400") and 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (manufactured by Kawaguchi Kagaku under the trade designation "Antage W-500"); bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (manufactured by Kawaguchi Kagaku under the trade designation "Antage W-300"), 4,4'-methylenebis(2,6-di-t-butylphenol) (manufactured by Laporte Performance Chemicals under the trade designation "Ionox 220AH"), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (bisphenol A), 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] (manufactured by Ciba Speciality Chemicals under trade designation "Irganox L109"), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate]

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(manufactured by Yoshitomi Seiyaku under the trade designation "Tominox 917"), 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by Ciba Speciality Chemicals under the trade designation "Irganox L115"), 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 (manufactured by Sumitomo Kagaku under the trade designation "Sumilyzer GA80"), 4,4'-thiobis(3-methyl-6-t-butylphenol) (manufactured by Kawaguchi Kagaku under the trade designation "Antage RC") and 2,2'-thiobis(4,6-di-t-butyl)resorcin; polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane (manufactured by Ciba Speciality Chemicals under the trade designation "Irganox L101"), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)-butane (manufactured by Yoshitomi Seiyaku under the trade designation "Yoshinox 930"), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (manufactured by Ciba Speciality Chemicals under the trade designation "Irganox 1330"), 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'-methylbenzyl)-4-methylphenol; and phenol-aldehyde condensates such as the condensate of p-t-butylphenol and formaldehyde and the condensate of p-t-butylphenol and acetaldehyde.

Examples of phosphorous-based antioxidants include triaryl phosphites such as triphenyl phosphite and tricresyl phosphite, trialkyl phosphites such as trioctadecyl phosphite and tridecyl phosphite, and tridodecyl trithiophosphite.

These antioxidants can be used individually, or a plurality can be used in combination, and the amount

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added thereof may conveniently be from 0.01 to 2.0 parts by weight per 100 parts by weight of base oil.

Examples of metal deactivators which can be used in the lubricant composition of the present invention

5 include benzotriazole, and benzotriazole derivatives, for example, 4-alkylbenzotriazoles such as 4-methylbenzotriazole and 4-ethylbenzotriazole, 5-alkylbenzotriazoles such as 5-methylbenzotriazole and 5-ethylbenzotriazole, 1-alkylbenzotriazoles such as 1-

10 dioctylaminomethyl-2,3-benzotriazole and 1-alkyltolutriazoles such as 1-dioctylaminomethyl-2,3-tolutriazole; benzimidazole, and benzimidazole derivatives, for example, 2-(alkyldithio)benzimidazoles such as 2-(octyldithio)benzimidazole, 2-

15 (decyldithio)benzimidazole and 2-(dodecyldithio)benzimidazole, and 2-(alkyldithio)-toluimidazoles such as 2-(octyldithio)toluimidazole, 2-decyldithio)toluimidazole and 2-(dodecyldithio)-toluimidazole; indazole, and indazole derivatives, for

20 example, toluindazoles such as 4-alkyl-indazole and 5-alkyl-indazole; benzothiazole, and benzothiazole derivatives, for example, 2-(alkyldithio)benzothiazoles such as 2-mercaptobenzothiazole derivative (manufactured by Chiyoda Kagaku under the trade designation "Thiolite

25 B-3100"), 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-

30 (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-dibutyl-

35 dithiocarbamyl)toluthiazole and 2-(N,N-dihexyldithiocarbamyl)toluthiazole; benzoxazole derivatives, for

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example, 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, for example, 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-thiazidazole, 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, for example, 1-alkyl-2,4-triazoles such as 1-dioctylaminomethyl-2,4-triazole.

These metal deactivators can be used individually, or a plurality can be used in combination, and the amount added thereof may conveniently be from 0.005 to 0.5 parts by weight per 100 parts by weight of base oil.

Examples of defoamers which can be used include organosilicates such as dimethylpolysiloxane, diethyl silicate and fluorosilicone, and non-silicone defoamers such as polyalkyl acrylates. These can be used individually or a plurality can be used in combination, and the amount added thereof may conveniently be from 0.0001 to 0.1 parts by weight per 100 parts by weight of base oil.

Examples of viscosity index improvers include non-dispersant-type viscosity index improvers for example, polymethacrylates and olefin copolymers such as

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ethylene/propylene copolymer and styrene/diene copolymer, and dispersion-type viscosity index improvers such as those obtained by copolymerizing these with nitrogen-containing monomers. The amount added thereof may conveniently be from 0.05 to 20 parts by weight per 100 parts by weight of base oil.

Examples of flow point depressors include polymethacrylate-based polymers. The amount added thereof may conveniently be from 0.01 to 5 parts by weight per 100 parts by weight of base oil.

Examples of detergent dispersants include metal-based detergents, for example, neutral or basic alkaline earth metal sulphonates, alkaline earth metal phenates and alkaline earth metal salicylates, and ashless dispersants, for example modified products obtained from alkenyl succinate imides, alkenyl succinate esters or boron compounds, sulphur compounds etc. thereof. These can be used individually or a plurality can be used in combination, and the amount added thereof may conveniently be from 0.01 to 1 parts by weight per 100 parts by weight of base oil.

Examples of extreme-pressure agents and friction regulators include sulphur-based extreme-pressure agents such as dialkyl sulphides, dibenzyl sulphide, dialkyl polysulphides, dibenzyl disulphide, alkyl mercaptans, dibenzothiophene and 2,2'-dithiobis(benzothiazole); phosphorous-based extreme-pressure agents such as trialkyl phosphates, trialkyl phosphonates, trialkyl phosphites, triaryl phosphites, dialkyl hydrogen phosphites, trialkyl trithiophosphites and triaryl phosphorothioates; aliphatic friction regulators such as fatty acid amides and fatty acid esters; amine-based friction regulators such as primary to tertiary alkylamines and alkylene oxide adducts of alkyl amines; and extreme-pressure agents such as zinc alkyl

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dithiophosphates. These extreme-pressure agents and friction regulators can be used individually, or a plurality can be used in combination, and the amount added thereof may conveniently be in the range from 0.05 to 5.0 parts by weight per 100 parts by weight of base oil.

5 Examples of rust preventers which can be used include N-alkylsarcosinic acids, alkylate phenoxy acetates, imidazolines, "KX1031" manufactured by King Industry and alkaline earth metal salts thereof and amine salts thereof, the N-acyl-N-alkoxyalkyl asparaginate esters disclosed in Japanese Unexamined Patent Application Number H6-200268, the alkaline earth metal salts of phosphate esters disclosed in EP-A-0801116 and alkenyl succinate ester-based rust preventers. These rust preventers can be used individually or a plurality can be used in combination, and the amount added may conveniently be in the range of from 0.005 to 1.0 parts by weight can be used per 100 parts by weight of base oil.

15 Examples of anti-emulsifying agents (used to break up emulsions to allow separation into two liquid layers) include commonly known substances which are usually used as lubricating oil additives, for example, polyalkylene glycol-based nonionic surfactants such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers and polyoxyethylene alkyl naphthyl ethers. The amount added may conveniently be in the range of from 0.0005 to 0.5 parts by weight per 100 parts by weight of base oil.

25 It is particularly appropriate to use the lubricating oil composition of the present invention as a hydraulic oil composition as described above. However, said lubricating oil composition can also be used in other ways, for example, as a compressor oil composition,

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turbine oil composition, bearing oil composition or gear oil composition.

The present invention will now be described with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

The present invention is described specifically below by means of hydraulic oil working examples.

Hydrogenation-purified base oil having a kinematic viscosity of 31 mm²/s at 40°C was used as the base oil, and the components shown below were added to yield base lubricating oil compositions.

The anti-wear agents shown in Tables 2, 3 and 4 were added to this base lubricating oil composition A (Table 1) to yield test oil having a kinematic viscosity of 32 mm²/s at 40°C.

The amount of the various additive components in the test oils of Working Examples 1 and 2 and Comparative Examples 1 to 10 are given as parts by weight with respect to the test oil.

TABLE 1

Base lubricating oil composition A	
Hydrogenation-purified base oil: Kinematic viscosity 31 mm ² /s @ 40°C	99.15 parts by weight
Antioxidant: (manufactured by Echiru under the trade designation "Hitec 4733")	0.5 parts by weight
Metal deactivator: (manufactured by Ciba Speciality Chemicals under the trade designation "Irgamet 39")	0.05 parts by weight
Flow point depressor: (manufactured by Toho Kagaku Kogyo under the trade designation "Lubran 141")	0.3 parts by weight

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Inventive lubricating oil composition (Working Examples 1 and 2) and conventional anti-wear compositions which do not comprise the inventive composition, by way of comparison, (Comparative Examples 1 to 6) were prepared according to the proportions shown in Tables 2 and 3.

The working example and comparative example compositions were subjected to vane pump tests as described below and the results are shown in Table 5.

Also, for comparison, the same performance appraisal tests were performed on commercial products obtained using the zinc-free ashless anti-wear hydraulic oils shown in Table 4 (Comparative Examples 7 and 8), and these results are also shown in Table 5. It should be noted that the methods for the performance tests performed on the working examples and comparative examples were as follows.

IP 281 "Vickers V104C" vane pump test

In order to appraise the anti-wear performance of the test oil in a vane pump, the pump test was formed for 250 h at a pressure of 13.73 MPa (140 kgf/cm²), 1500 rpm, oil temperature 65°C using a "Vickers V104C" pump, and the wear of the vane and ring were measured after the test. The DIN 51524 (part 2) criterion for anti-wear hydraulic oil is that the total amount of wear on the vane and ring be equivalent to no more than 150 mg.

"Vickers 35VQ-25A" vane pump test

In order to appraise the anti-wear performance of the test oil in a vane pump at high pressure, high speed and high temperature, the pump test was performed for 50 h at a pressure of 20.59 MPa (210 kgf/cm²), 2400 rpm, oil temperature 93°C using a "Vickers 35VQ-25A" pump, and the wear on the vane and ring was measured after the test. The "Vickers" M-2950-S criterion is that the vane wear be

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equivalent to no more than 15 mg and the ring wear be equivalent to no more than 75 mg.

The "General Motors" LS-2 LH.03.04.06 criteria are stricter: vane wear corresponding to no more than 10 mg
 5 and ring wear corresponding to no more than 50 mg.

TABLE 2

Example	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Base lubricating oil composition A (% by weight)	100	99.5	99.0	99.0
Component 1 β -dithiophos- phorylated propionic acid	-	-	-	-
Component 2 Trialkyl phenyl phosphate ester	-	0.5	1.0	-
Triphenyl phosphoro-thioate	-	-	-	1.0

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TABLE 3

Example	Working Example 1	Working Example 2	Comparative Example 5	Comparative Example 6
Base lubricating oil composition A(% by weight)	99.18	99.18	99.975	99.48
Component 1 β -dithiophospho- rylated propionic acid	0.02	-	0.025	0.02
Component 2 Trialkyl phenyl phosphate ester	0.8	0.8	-	-
Component 3 β -dithiophospho- rylated propionic acid	-	0.02	-	-
Triphenylphospho- thioate	-	-	-	0.5

In Tables 2 and 3 above, Component 1 is a β -
dithiophosphorylated propionic acid represented by
5 general formula (1) in which R¹ is an isobutyl group and
R² is a methyl group.

Component 2 in Tables 2 and 3 is a triarylphosphate
sold under the trade designation "Reofos 65" ex.
Ajinomoto.

10 Component 3 is a β -dithiophosphorylated propionic
acid represented by the general formula (1) in which R¹
is an isobutyl group and R² is a hydrogen group.

Triphenylphosphorothioate in Table 3 is that sold
under the trade designation "Irgalube TPPT" ex. Ciba.

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TABLE 4

Commercial anti-wear hydraulic oil	Comparative Example 7	Comparative Example 8
Phosphorus content (% by weight)	0.163	0.092
Sulphur content (% by weight)	-	0.020
Kinematic viscosity cSt 40°C	30.6	30.4
Kinematic viscosity cSt 100°C	5.46	5.29

Note: All commercial anti-wear hydraulic oils used were zinc free.

TABLE 5

Example	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Working Ex. 1	Working Ex. 2
IP 281 "Vickers VI04C"										
Vane Pump Test										
vane wear (mg)	49	37	8	6	3	8	45	9	2	3
Ring wear (mg)	415	213	65	34	3	159	40	36	3	1
Total wear (mg)	464	250	73	40	6	167	85	45	5	4
"Vickers 35VQ25A" Vane										
Pump Test										
vane wear (mg)	-	-	38	8	3	-	22	39	2	2
Ring wear (mg)	-	-	606	108	7	-	351	755	3	2
Total wear (mg)	-	-	644	116	10	-	373	794	5	4

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Comparative Examples 1 and 2 did not exhibit adequate anti-wear properties in the "Vickers V104C" vane pump test and did not have the anti-wear properties required to pass German Standard DIN 51524 (part 2).

5 Comparative Examples 3 and 4 did pass German Standard DIN 51524 (part 2) in the "Vickers V104C" vane pump test, but did not exhibit adequate anti-wear properties in the "Vickers 35VQ25A" vane pump test and did not pass the "Vickers" M-2950-S standard or "General Motors" LS-2
10 LH.03.04.06 standard. Comparative Examples 7 and 8 exhibited anti-wear properties sufficient to pass German Standard DIN 51524 (part 2) in the V104C vane pump test, but their anti-wear properties were not sufficient to pass the "Vickers" M-2950-S standard or the "General
15 Motors" LS-2-LH.03.04.06 standard.

As is clear from the compositions shown in Table 3 and the results shown in Table 5, the lubricating oil composition according to the present invention (Working
20 Examples 1 and 2) have excellent anti-wear properties sufficient to pass German Standard DIN 51524 (Part 2), "Vickers" M-2950-S standard and "General Motors" LS-2 LH.03.04.06 standard, in vane pump tests "Vickers" V104C and 35VQ25A, and their lubricating oil performance is
25 sufficient for use as a hydraulic oil in high-pressure applications. Comparative Example 5 shows increased total wear in both tests when compared to Working Examples 1 and 2.

However, when the additive combination of the present invention is not used (comparative examples), and
30 in the case of commercial zinc-free hydraulic oils and zinc-based hydraulic oils, the anti-wear properties and extreme-pressure performance are both considerably poorer and there are problems when these oils are used as lubricating oils for modern industrial machines which

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have been miniaturized and work at high speeds, high pressures and high precision.

Comparative Examples 9 and 10

5 Comparative Examples 9 and 10 were performed in order to see whether the thermal oxidative stability is better when R² in the β -dithiophosphorylated propionic acid is hydrogen or when it is a methyl group. The composition and results for Comparative Examples 9 and 10 are shown in Table 6.

10 The thermal oxidative stability test was performed as follows: 200 ml of test oils of Comparative Examples 9 and 10, obtained by combining β -dithiophosphorylated propionic acid and antioxidant and rust preventer, were independently introduced into 250 ml beakers, a steel
15 sample and copper sample of diameter 0.6 mm and length 7.6 mm, which had been polished using # 240 alumina polishing paper, washed and dried, were intersected and the test oils were applied thereto, and the test oils were subjected to thermal oxidative deterioration for 336
20 hours in a 140°C oven, and after the test the test oils were suction-filtered using a 0.8 μ m hole diameter filter and the amount of sludge obtained, the external appearance of the copper sample and steel sample and the colour of the test oil (ASTM D1500) were measured.

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TABLE 6

	Comparative Example 9	Comparative Example 10
Hydrogenated purified base oil B *1	99.74	99.74
Antioxidant *2	0.10	0.10
Rust preventer *3	0.01	0.01
β -dithiophosphorylated propionic acid R ¹ : isobutyl R ² : hydrogen	0.15	-
β -dithiophosphorylated propionic acid R ¹ : isobutyl R ² : methyl	-	0.15
Colour of test oil	L 0.5	L 0.5
Thermal oxidation stability test	L 5.0	L 4.5
Colour of oil		
Appearance of copper	No rust	No rust
Appearance of steel	No change	No change
Amount of sludge (mg)	10.3	0.0

- *1 Hydrogenated purified base oil B: kinematic
viscosity 32 Cst (at 40°C),
Sulphur content no greater than 5 ppm, viscosity
index 110
- *2 Antioxidant: under the trade designation "Irganox
L135": manufactured by Ciba Speciality Chemicals
- *3 Rust preventer: under the trade designation "IRGAMET
39", manufacture by Ciba Speciality Chemicals

As is clear from the results of the thermal
oxidative stability tests shown in Table 6, the compound
of Comparative Example 10 in which one of the hydrogen
atoms on the α -carbon of the β -dithiophosphorylated
propionic acid has been substituted by an alkyl group,
undergoes less change in colour and produces less sludge,
that is, is more stable, than the compound of Comparative
Example 9 in which there is no alkyl substitution of the

hydrogen atoms on the α -carbon. If there are too many carbon atoms in the alkyl group substitutions on the α -carbon, anti-wear properties deteriorate and so, in order to achieve both thermal oxidative stability and anti-wear properties, the alkyl group substituent is most preferably a methyl group.

Additional experimental data is shown below which demonstrates that examples of the formulations of the present invention comprising base oil, β -dithiophosphorylated propionic acid (A) and triaryl phosphate (B) surprisingly display advantageous anti-wear properties relative to formulations which comprise combinations of base oil, β -dithiophosphorylated propionic acid and triarylphosphorothionate antiwear additive.

It should be noted that in Comparative Example 13, the addition of 0.8 % wt of triphenylphosphorothionate compared to the formulation of Comparative Example 11 adversely affects the Amsler Wear Rate. In contrast, the addition of an identical amount of triaryl phosphate ester in Working Example 4 not only has no adverse affect on the Amsler Wear Rate, but actually **improves** the Amsler Wear Rate compared to the

formulation of Comparative Example 11.

Component	Working Example 3	Working Example 4	Comparative Example 11	Comparative Example 12	Comparative Example 13
Base lubricating oil formulation ¹ (% wt)	99.48	99.18	99.98	99.48	99.18
β -dithiophosphorylated propionic acid ² (% wt)	0.02	0.02	0.02	0.02	0.02
Triaryl phosphate ester ³ (% wt)	0.50	0.80	-	-	-
Triphenylphosphorothionate ⁴ (% wt)	-	-	-	0.50	0.80
TOTAL	100	100	100	100	100
Amsler Wear Rate	2.43	2.72	2.97	2.52	3.90

¹ Base lubricating oil formulation containing 0.05% wt of metal passivator, 0.10% wt of aminic antioxidant, 0.40% wt of phenolic antioxidant, 0.30% wt of pour point depressant and 99.15% wt of Group II base oil, based on the total weight of said base lubricating oil formulation.

² Additive available under the trade designation "IRGALUBE 353" from Ciba Speciality Chemicals.

³ Additive available under the trade designation "DURAD 150" from Great Lakes Chemical Corporation.

⁴ Additive available under the trade designation "IRGALUBE TPPT" from Ciba Speciality Chemicals.

Advantages of the Present Invention

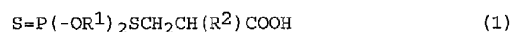
Lubricating oil compositions of the present invention contain no, or almost no, ash-forming substances such as zinc dialkyl dithiophosphates, in view of environmental and safety considerations; the resulting anti-wear lubricating oil compositions exhibit
5 excellent anti-wear with respect to various machine elements even when used under severe high pressure, high speed and high load conditions. Accordingly, the lubricating oil compositions of the present invention are highly effective in the provision of lubricating oil which can guarantee the reliability of equipment over long periods, in
10 response to the recently developed, high pressure and high precision industrial machines.

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C L A I M S

1. Lubricating oil composition, comprising β -dithiophosphorylated propionic acid (A), triaryl phosphate (B) and base oil comprising mineral oil and/or synthetic oil.

5 2. Lubricating oil composition according to Claim 1, wherein the β -dithiophosphorylated propionic acid (A) is represented by the general formula (1) below:-



wherein R^1 , which may be identical or different,
10 represents a branched alkyl group of from 3 to 8 carbon atoms and R^2 represents a hydrogen atom or alkyl group of from 1 to 4 carbon atoms.

3. Lubricating oil composition according to Claim 2, where R^2 is a methyl group, ethyl group or hydrogen
15 group.

4. Lubricating oil composition according to any one of Claims 1 to 3, wherein the β -dithiophosphorylated propionic acid (A) is selected from
3-(O,O-diisopropyldithiophosphoryl)propionic acid,
20 3-(O,O-diisopropyldithiophosphoryl)-2-methyl-propionic acid, 3-(O,O-diisobutyldithiophosphoryl)-propionic acid and 3-(O,O-diisobutyldithiophosphoryl)-2-methyl-propionic acid.

5. Lubricating oil composition according to any one of
25 Claims 1 to 4, in which from 0.001 to 1.0 % by weight of β -dithiophosphorylated propionic acid (A) is incorporated therein, with respect to the total amount of lubricating oil composition.

6. Lubricating oil composition according to any one of
30 Claims 1 to 5, in which from 0.001 to 0.5% by weight of

β -dithiophosphorylated propionic acid (A) is incorporated therein, with respect to the total amount of lubricating oil composition.

7. Lubricating oil composition according to any one of claims 1 to 6, wherein the triaryl phosphate (B) is represented by the general formula (2) below:



wherein each R^3 is, independently, a phenyl group or a phenyl group having alkyl group(s) of from 1 to 9 carbon atoms.

8. Lubricating oil composition according to any one of claims 1 to 7, in which from 0.05 to 10% by weight of triaryl phosphate (B) is incorporated therein, with respect
10 to the total amount of lubricating oil composition.

9. Lubricating oil composition according to any one of claims 1 to 8, in which from 0.05 to 5% by weight of triaryl phosphate (B) is incorporated therein, with respect to the total amount of lubricating oil composition.

10. Lubricating oil composition substantially as hereinbefore described with
15 reference to any one of the examples but excluding the comparative examples.

11. Use of a lubricating oil composition according to any one of claims 1 to 10, in a hydraulic machine, a compressor, a turbine, a bearing and/or a gear.

12. Use of a lubricating oil composition substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples

Dated 26 July, 2006

Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON