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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 November 2014 (20.11.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/184068 A1

(51) International Patent Classification:
C10M 105/36 (2006.01) *C10N 40/02* (2006.01)
C10M 129/72 (2006.01) *C10N 40/04* (2006.01)
C10N 30/06 (2006.01) *C10N 40/25* (2006.01)

(21) International Application Number:
PCT/EP2014/059338

(22) International Filing Date:
7 May 2014 (07.05.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13167627.2 14 May 2013 (14.05.2013) EP
13181269.5 22 August 2013 (22.08.2013) EP

(71) Applicant: BASF SE [DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors: SCHERER, Markus; Augartenstrasse 20, 68165 Mannheim (DE). **GOYAL, Arjun**; 1434 Windsor Drive, West Deptford, 08086 (US). **ECORMIER, Muriel**; H1, 1-2, 68159 Mannheim (DE). **BREITSCHEIDEL, Boris**; Goethestr. 72, 67165 Waldsee (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2014/184068 A1

(54) Title: LUBRICATING OIL COMPOSITION WITH ENHANCED ENERGY EFFICIENCY

(57) Abstract: The presently claimed invention is directed to a method for reducing the friction coefficient of a lubricating oil composition in the lubrication of a mechanical device comprising formulating said lubricating oil composition with a carboxylic acid ester obtainable by reacting a mixture comprising at least on dicarboxylic acid and at least one branched C_{10} alcohol.

Lubricating oil composition with enhanced energy efficiency

The presently claimed invention is directed to a method for reducing the friction coefficient of a lubricating oil composition in the lubrication of a mechanical device comprising formulating said lubricating oil composition with a carboxylic acid ester obtainable by reacting a mixture comprising at least on dicarboxylic acid and at least one branched C_{10} alcohol.

The commercially available lubricating oil compositions are produced from a multitude of different natural or synthetic components. To improve the required properties, according to the field of use, further additives are usually added. The base oils often consist of mineral oils, highly refined mineral oils, alkylated mineral oils, poly-alpha-olefins (PAOs), polyalkylene glycols, phosphate esters, silicone oils, diesters and esters of polyhydric alcohols.

The different lubricants, such as motor oil, turbine oil, hydraulic fluid, transmission oil, compressor oil and the like, must satisfy extremely high criteria such as high viscosity index, good lubricant performance, high oxidation stability, good thermal stability or comparable properties.

High-performance lubricant oil formulations which are used as transmission, industrial or motor oils are oils with a special performance profile with regard to shear stability, low-temperature viscosity, long service life, evaporation loss, fuel efficiency, seal compatibility and wear protection. Such oils are currently being formulated preferentially with PAO (especially PAO 6) or group I, II or Group III mineral oils as carrier fluids, and with specific polymers (polyisobutylenes = PIBs, olefin copolymers = ethylene/propylene copolymers=OCPs, polyalkyl methacrylates = PMAs) as thickeners or viscosity index improvers in addition to the customary additive components. Together with PAOs, low-viscosity esters are typically being used, for example DIDA (diisodecyl adipate), DITA (diisotridecyl adipate) or TMTC (trimethylolpropane caprylate), especially as solubilizers for polar additive types and for optimizing seal compatibilities.

Esters are used as co-solvent, especially in motor oil, turbine oil, hydraulic fluid, transmission oil, compressor oil, but esters are also used as base oils, in which they are the main component.

EP 0 767 236 AI discloses a gear lubricating oil composition. The composition contains more than 20 % by volume a hydrogenated polyalphaolefin, and less than 80 % by volume of mineral oil or synthetic ester oil or a combination thereof. The examples contain 10 % by volume bis(tridecyl)-adipate.

WO 98/04658 A1 discloses base stocks for synthetic gear oils for use in heavy and medium duty axle gear lubricants and transmission fluid application. The lubricant disclosed therein contains 1 % to 20 % by weight of an ester. The ester includes diesters of C_{8-13} adipates, in particular diisodecyl adipate.

US Patent 4,370,247 discloses a gear or axle lubricant containing 25 to 60 mass % of at least one di-C_{8-12} alkyl ester of a dicarboxylic acid. The whole lubricant disclosed therein is reported to decrease power loss due to friction, therefore conserving fuel consumption.

CA 2 637 401 discloses a variety of diesters derived from a dicarboxylic acid having 2 to 36 carbon atoms and a branched alcohol having 4 to 40 carbon atoms. The lubricants can contain 0.1 to 100% by weight, or 5 to 99% by weight of the diesters.

WO 2011/34829 A1 discloses a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition comprising C_{4-30} diester of adipic acid.

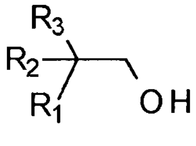
Although different lubricants, such as motor oil, turbine oil, hydraulic fluid, transmission oil, compressor oil and the like, satisfy extremely high criteria such as high viscosity index, good lubricant performance, high oxidation stability and good thermal stability, there is still a need to reduce the amount of energy consumed in operation of mechanical devices.

Thus, it was an object of the presently claimed invention to provide a method that allows for operating mechanical devices at lower energy consumption.

The object was met by providing a method for reducing the friction coefficient of a lubricating oil composition in the lubrication of a mechanical device comprising formulating said lubricating oil composition with a carboxylic acid ester obtainable by reacting a mixture comprising

a) at least one dicarboxylic acid, optionally in form of its anhydride, and

b1) at least one monoalcohol having 10 carbon atoms and a structure of general formula I,



I,

wherein R^1 is pentyl, R^2 is H and R^3 is propyl.

By the term lubricating oil composition, in the sense of the presently claimed invention, is meant a substance capable of reducing friction between moving surfaces.

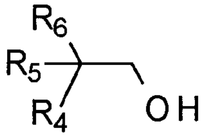
The friction-modification properties are determined by measuring the friction coefficient at 25% slide roll ratio (SRR) using mini-traction machine (MTM) measurements at 70 °C and 1 GPa. Reducing the friction coefficient means in the sense of the presently claimed invention that the friction coefficient of a lubricating oil composition comprising a carboxylic acid ester as defined above is lower than the friction coefficient of a lubricating oil composition that does not contain said carboxylic acid ester.

A mechanical device in the sense of the presently claimed invention is a mechanism consisting of a device that works on mechanical principles.

Preferably the dicarboxylic acid is selected from the group consisting of phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, glutaric acid, diglycolic acid, 1,4-cyclohexanedicarboxylic acid, 2,6-decahydronaphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid and 2,5-norbornanedicarboxylic acid. More preferably the dicarboxylic acid is selected from the group consisting of glutaric acid, diglycolic acid, succinic acid, azelaic acid, sebacic acid, 1,4-cyclohexanedicarboxylic acid, adipic acid, 2,6-decahydronaphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid and 2,5-norbornanedicarboxylic acid. Most preferably the aliphatic dicarboxylic acid is adipic acid.

The dicarboxylic acids can be used either in pure form or in the form of mixtures with monocarboxylic acids. Instead of the dicarboxylic acids, their anhydrides can also be used. Representative monocarboxylic acids include n-butanoic acid, n-pentanoic acid, n-hexanoic acid, n-heptanoic acid, n-octanoic acid, n-nonanoic acid, n-decanoic acid, isobutanoic acid, isopentanoic acid, isohexanoic acid, isoheptanoic acid, isooctanoic acid, 2-ethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, and isodecanoic acid.

Preferably the mixture further comprises a monoalcohol b2) having 10 carbon atoms and a structure of the general formula II,



II,

wherein

R_4 is selected from the group consisting of pentyl, iso-pentyl, 2-methyl-butyl, 3-methyl-butyl and 2,2-dimethyl-propyl,

R_5 is H or methyl and

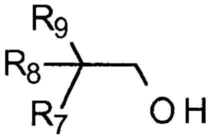
R_6 is selected from the group consisting of ethyl, propyl and iso-propyl,

whereby the monoalcohol b1) and the monoalcohol b2) have a different structure.

Preferably the monoalcohol b2) is selected from the group consisting of 2-propyl-4-methyl-hexanol, 2-propyl-5-methyl-hexanol, 2-isopropyl-4-methyl-hexanol, 2-isopropyl-5-methyl-hexanol, 2-propyl-4,4-dimethylpentanol, 2-ethyl-2,4-dimethylhexanol, 2-ethyl-2-methyl-heptanol, 2-ethyl-2,5-dimethylhexanol and 2-isopropyl-heptanol. More preferably the monoalcohol b2) is 2-propyl-4-methyl-hexanol.

Preferably the weight ratio of monoalcohol b1) to monoalcohol b2) is in the range of 5:1 to 95:1, more preferably in the range of 6:1 to 50:1, even more preferably in the range of 10:1 to 40:1, most preferably in the range of 20:1 to 35:1.

Preferably the mixture further comprises a monoalcohol b3) having 10 carbon atoms and a structure of the general formula III,



III,

wherein

R_7 is selected from the group consisting of pentyl, iso-pentyl, 2-methyl-butyl, 3-methyl-butyl and 2,2-dimethyl-propyl,

R_8 is H or methyl,

R_9 is selected from the group consisting of ethyl, propyl and iso-propyl.

Preferably the monoalcohol b3) has a different structure from both the monoalcohol b1) and the monoalcohol b2). Preferably the monoalcohol b3) is selected from the group consisting of 2-propyl-5-methyl-hexanol, 2-isopropyl-4-methyl-hexanol, 2-isopropyl-5-methyl-hexanol, 2-propyl-4,4-dimethylpentanol, 2-ethyl-2,4-dimethylhexanol, 2-ethyl-2-methyl-heptanol, 2-ethyl-2,5-dimethylhexanol and 2-isopropyl-heptanol. More preferably the monoalcohol b3) is 2-propyl-5-methyl-hexanol.

Preferably the mixture comprises 80 to 95 weight-% of 2-n-propyl-heptanol as component b1), 1.0 to 10 weight.% of 2-propyl-4-methyl-hexanol as component b2), 1.0 to 10 weight- % of 2-propyl-5-methyl-hexanol as component b3) and 0.1 to 2.0 weight-% of 2-isopropyl-heptanol, whereby the weight of each component is related to the total weight of the monoalcohols. More preferably the mixture comprises 91.0 to 95.0 weight-% of 2-n-propyl-heptanol as component b1), 2.0 to 5.0 weight-% of 2-propyl-4-methyl-hexanol as component b2), 3.0 to 5.0 weight-% of 2-propyl-5-methyl-hexanol as component b3) and 0.1 to 0.8 weight-% of 2-isopropyl-heptanol, whereby the weight of each component is related to the total weight of the monoalcohols.

Preferably the monoalcohol b1) is present in a molar ratio in the range of 2.05:1 to 3.0:1 in relation to the acid a), more preferably in the range of 2.1:1 to 2.5:1.

Preferably the lubricating oil composition comprises ≥ 1 % to ≤ 10 % by weight or ≥ 1 % to ≤ 40 % by weight or ≥ 20 % to ≤ 100 % by weight,
more preferably ≥ 1 % to ≤ 5 % by weight or ≥ 1 % to ≤ 35 % by weight or ≥ 25 % to ≤ 100 % by weight, most preferably ≥ 1 % to ≤ 2 % by weight or ≥ 2 % to ≤ 30 % by weight or ≥ 30 % to ≤

100 % by weight of at least one carboxylic acid ester as defined above, related to the total amount of the lubricating oil composition.

Preferably the lubricating oil composition further comprises further base stocks selected from the group consisting of mineral oils (Gr I, II or III oils), polyalphaolefins, polymerized and interpolymerized olefins, alkyl naphthalenes, alkylene oxide polymers, silicone oils, phosphate esters and carboxylic acid esters. Preferably the lubricating oil comprises ≥ 50 % to ≤ 99 % by weight or ≥ 80 % to ≤ 99 % by weight or ≥ 90 % to ≤ 99 % by weight base stocks, related to the total amount of the lubricating oil composition.

Definitions for the base stocks in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in the following table

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in the following table

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in the following table

Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

Synthetic lower viscosity fluids suitable for the presently claimed invention include the polyalphaolefins (PAOs) and the synthetic oils from the hydrocracking or hydroisomerization of Fischer Tropsch high boiling fractions including waxes. These are both stocks comprised of saturates with low impurity levels consistent with their synthetic origin. The hydroisomerized Fischer Tropsch waxes are highly suitable base stocks, comprising saturated components of iso-paraffinic character (resulting from the isomerization of the predominantly n-paraffins of the Fischer Tropsch waxes) which give a good blend of high viscosity index and low pour point. Processes for the hydroisomerization of Fischer Tropsch waxes are described in U.S. Patents 5,362,378; 5,565,086; 5,246,566 and 5,135,638, as well in EP 710710, EP 321302 and EP 321304.

Polyalphaolefins suitable for the presently claimed invention, as either lower viscosity or high viscosity fluids depending on their specific properties, include known PAO materials which typically comprise relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include but are not limited to C_2 to about C_{32} alphaolefins with the C_8 to about C_{16} alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene, and poly-1-dodecene, although the dimers of higher olefins in the range of C_{14} to C_{18} provide low viscosity base stocks.

Low viscosity PAO fluids suitable for the presently claimed invention, may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example, the methods disclosed by U.S. Patents 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patents: 3,742,082 (Brennan); 3,769,363 (Brennan); 3,876,720 (Heilman); 4,239,930 (Allphin); 4,367,352 (Watts); 4,413,156 (Watts); 4,434,408 (Larkin); 4,910,355 (Shubkin); 4,956,122 (Watts); and 5,068,487 (Theriot).

Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2- ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulphides and derivative, analogs and homologs thereof.

Further carboxylic acid esters suitable for the presently claimed invention include the esters of mono and polybasic acids with monoalkanols (simple esters) or with mixtures of mono and polyalkanols (complex esters), and the polyol esters of monocarboxylic acids (simple esters), or mixtures of mono and polycarboxylic acids (complex esters). Esters of the mono/polybasic type include, for example, the esters of monocarboxylic acids such as heptanoic acid, and dicarboxylic acids such as phthalic acid, succinic acid, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, or mixtures thereof with polyalkanols, etc. Specific examples of these types of esters include nonyl heptanoate, dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacatediisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, dibutyl -TMP- adipate, etc.

Also suitable for the presently claimed invention are esters, such as those obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols, e.g. neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol with monocarboxylic acids containing at least 4 carbons, normally the C_5 to C_{30} acids such as saturated straight chain fatty acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures thereof, with polycarboxylic acids.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters and C_{13} Oxo acid diester of tetraethylene glycol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2- ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, oly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

The lubricating oil composition of the invention optionally further includes at least one other performance additive. The other performance additives include dispersants, metal deactivators, detergents, viscosity modifiers, extreme pressure agents (typically boron- and/or sulphur- and/or phosphorus- containing), antiwear agents, antioxidants (such as hindered phenols, aminic antioxidants or molybdenum compounds), corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, friction modifiers and mixtures thereof.

The total combined amount of the other performance additives (excluding the viscosity modifiers) present on an oil free basis may include ranges of 0 % by weight to 25 % by weight, or 0.01 % by weight to 20 % by weight, or 0.1 % by weight to 15 % by weight or 0.5 % by weight to 10 % by weight, or 1 to 5 % by weight of the composition.

Although one or more of the other performance additives may be present, it is common for the other performance additives to be present in different amounts relative to each other.

In one embodiment the lubricating composition further includes one or more viscosity modifiers.

When present the viscosity modifier may be present in an amount of 0.5 % by weight to 70 % by weight, 1 % by weight to 60 % by weight, or 5 % by weight to 50 % by weight, or 10 % by weight to 50 % by weight of the lubricating composition.

Viscosity modifiers include (a) polymethacrylates, (b) esterified copolymers of (i) a vinyl aromatic monomer and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, (c) esterified interpolymers of (i) an alpha-olefin; and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, or (d) hydrogenated copolymers of styrene-butadiene, (e) ethylene-propylene copolymers, (f) polyisobutenes, (g) hydrogenated styrene-isoprene polymers, (h) hydrogenated isoprene polymers, or (i) mixtures thereof.

In one embodiment the viscosity modifier includes (a) a polymethacrylate, (b) an esterified copolymer of (i) a vinyl aromatic monomer; and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, (c) an esterified interpolymer of (i) an alpha-olefin; and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, or (d) mixtures thereof.

Extreme pressure agents include compounds containing boron and/or sulphur and/or phosphorus.

The extreme pressure agent may be present in the lubricating composition at 0 % by weight to 20 % by weight, or 0.05 % by weight to 10 % by weight, or 0.1 % by weight to 8 % by weight of the lubricating composition.

In one embodiment the extreme pressure agent is a sulphur- containing compound. In one embodiment the sulphur-containing compound may be a sulphurised olefin, a polysulphide, or mixtures thereof. Examples of the sulphurised olefin include a sulphurised olefin derived from propylene, isobutylene, pentene; an organic sulphide and/or polysulphide including benzyldisulphide; bis-(chlorobenzyl) disulphide; dibutyl tetrasulphide; di-tertiary butyl polysulphide; and sulphurised methyl ester of oleic acid, a sulphurised alkylphenol, a sulphurised dipentene, a sulphurised terpene, a sulphurised Diels-Alder adduct, an alkyl sulphenyl N'N- dialkyl dithiocarbamates; or mixtures thereof.

In one embodiment the sulphurised olefin includes a sulphurised olefin derived from propylene, isobutylene, pentene or mixtures thereof.

In one embodiment the extreme pressure agent sulphur-containing compound includes a dimercaptothiadiazole or derivative, or mixtures thereof. Examples of the dimercaptothiadiazole include compounds such as 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof. The oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically form by forming a sulphur-sulphur bond between 2,5-dimercapto-1,3,4-thiadiazole units to form derivatives or oligomers of two or more of said thiadiazole units. Suitable 2,5-dimercapto-1,3,4-thiadiazole derived compounds include for example 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole or 2-tert-nonyldithio-5-mercapto-1,3,4-thiadiazole. The number of carbon atoms on the hydrocarbyl substituents of the hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically include 1 to 30, or 2 to 20, or 3 to 16.

In one embodiment the dimercaptothiadiazole may be a thiadiazole-functionalised dispersant. A detailed description of the thiadiazole- functionalised dispersant is described is paragraphs [0028] to [0052] of International Publication WO 2008/014315.

The thiadiazole-functionalised dispersant may be prepared by a method including heating, reacting or complexing a thiadiazole compound with a dispersant substrate. The thiadiazole compound may be covalently bonded, salted, complexed or otherwise solubilised with a dispersant, or mixtures thereof.

The relative amounts of the dispersant substrate and the thiadiazole used to prepare the thiadiazole-functionalised dispersant may vary. In one embodiment the thiadiazole compound is present at 0.1 to 10 parts by weight relative to 100 parts by weight of the dispersant substrate. In different embodiments the thiadiazole compound is present at greater than 0.1 to 9, or greater than 0.1 to less than 5, or 0.2 to less than 5: to 100 parts by weight of the dispersant substrate. The relative amounts of the thiadiazole compound to the dispersant substrate may also be expressed as (0.1-10):100, or (>0.1-9):100, (such as (>0.5-9):100), or (0.1 to less than 5): 100, or (0.2 to less than 5): 100.

In one embodiment the dispersant substrate is present at 0.1 to 10 parts by weight relative to 1 part by weight of the thiadiazole compound. In different embodiments the dispersant substrate is present at greater than 0.1 to 9, or greater than 0.1 to less than 5, or about 0.2 to less than 5: to 1 part by weight of the thiadiazole compound. The relative amounts of the dispersant substrate to the thiadiazole compound may also be expressed as (0.1-10):1, or (>0.1-9):1, (such as (>0.5-9):1), or (0.1 to less than 5): 1, or (0.2 to less than 5): 1.

The thiadiazole-functionalised dispersant may be derived from a substrate that includes a succinimide dispersant (for example, N-substituted long chain alkenyl succinimides, typically a polyisobutylene succinimide), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant, a polyetheramine dispersant, a viscosity modifier containing dispersant functionality (for example polymeric viscosity index modifiers (VMs) containing dispersant functionality), or mixtures thereof. In one embodiment the dispersant substrate includes a succinimide dispersant, an ester-containing dispersant or a Mannich dispersant.

In one embodiment the extreme pressure agent includes a boron- containing compound. The boron-containing compound includes a borate ester (which in some embodiments may also be referred to as a borated epoxide), a borated alcohol, a borated dispersant, a borated phospholipid or mixtures thereof. In one embodiment the boron-containing compound may be a borate ester or a borated alcohol.

The borate ester may be prepared by the reaction of a boron compound and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. The alcohols include dihydric alcohols, trihydric alcohols or higher alcohols, with the proviso for one embodiment that hydroxyl groups are on adjacent carbon atoms, i.e., vicinal.

Boron compounds suitable for preparing the borate ester include the various forms selected from the group consisting of boric acid (including metaboric acid, orthoboric acid and tetraboric acid), boric oxide, boron trioxide and alkyl borates. The borate ester may also be prepared from boron halides.

In one embodiment suitable borate ester compounds include tripropyl borate, tributyl borate, tripentyl borate, trihexyl borate, triheptyl borate, trioctyl borate, trinonyl borate and tridecyl borate. In one embodiment the borate ester compounds include tributyl borate, tri-2-ethylhexyl borate or mixtures thereof.

In one embodiment, the boron-containing compound is a borated dispersant, typically derived from an N-substituted long chain alkenyl succinimide. In one embodiment the borated dispersant includes a polyisobutylene succinimide. Borated dispersants are described in more detail in US Patents 3,087,936; and Patent 3,254,025.

In one embodiment the borated dispersant may be used m combination with a sulphur-containing compound or a borate ester.

In one embodiment the extreme pressure agent is other than a borated dispersant.

The number average molecular weight of the hydrocarbon from which the long chain alkenyl group was derived includes ranges of 350 to 5000, or 500 to 3000, or 550 to 1500. The long chain alkenyl group may have a number average molecular weight of 550, or 750, or 950 to 1000.

The N-substituted long chain alkenyl succinimides are borated using a variety of agents including boric acid (for example, metaboric acid, orthoboric acid and tetraboric acid), boric oxide, boron trioxide, and alkyl borates. In one embodiment the borating agent is boric acid which may be used alone or in combination with other borating agents.

The borated dispersant may be prepared by blending the boron compound and the N-substituted long chain alkenyl succinimides and heating them at a suitable temperature, such as, 80 °C to 250 °C, or 90 °C to 230 °C, or 100 °C to 210 °C, until the desired reaction has occurred. The molar ratio of the boron compounds to the N-substituted long chain alkenyl succinimides may have ranges including 10:1 to 1:4, or 4:1 to 1:3; or the molar ratio of the boron compounds to the N-substituted long chain alkenyl succinimides may be 1:2. Alternatively, the ratio of moles B : moles N (that is, atoms of B : atoms of N) in the borated dispersant may be 0.25:1 to 10:1 or 0.33:1 to 4:1 or 0.2:1 to 1.5:1, or 0.25:1 to 1.3:1 or 0.8:1 to 1.2:1 or about 0.5:1 An inert liquid may be used in performing the reaction. The liquid may include toluene, xylene, chlorobenzene, dimethylformamide or mixtures thereof.

In one embodiment the lubricating composition further includes a borated phospholipid. The borated phospholipid may be derived from boronation of a phospholipid (for example boronation may be carried out with boric acid). Phospholipids and lecithins are described in detail in Encyclopedia of Chemical Technology, Kirk and Othmer, 3rd Edition, in "Fats and Fatty Oils", Volume 9, pages 795-831 andin "Lecithins", Volume 14, pages 250-269.

The phospholipid may be any lipid containing a phosphoric acid, such as lecithin or cephalin, or derivatives thereof. Examples of phospholipids include phosphatidylcholine, phosphatidylserine, phosphatidylinositol, phosphatidylethanolamine, phosphotidic acid and mixtures thereof. The phospholipids may be glycerophospholipids, glycero derivatives of the above list of phospholipids. Typically, the glycerophospholipids have one or two acyl, alkyl or alkenyl groups on a glycerol residue. The alkyl or alkenyl groups may contain 8 to 30, or 8 to 25, or 12 to 24 carbon atoms. Examples of suitable alkyl or alkenyl groups include octyl, dodecyl, hexadecyl, octadecyl,docosanyl, octenyl, dodecenyl, hexadecenyl and octadecenyl.

Phospholipids may be prepared synthetically or derived from natural sources. Synthetic phospholipids may be prepared by methods known to those in the art. Naturally derived phospholipids are often extracted by procedures known to those in the art. Phospholipids may be derived from animal or vegetable sources. A useful phospholipid is derived from sunflower seeds. The phospholipid typically contains 35 % to 60 % phosphatidylcholine, 20 % to 35 % phosphatidylinositol, 1 % to 25 % phosphatidic acid, and 10 % to 25 % phosphatidylethanolamine, wherein the percentages are by weight based on the total phospholipids. The fatty acid content may be 20 % by weight to 30 % by weight palmitic acid, 2 % by weight to 10 % by weight stearic acid, 15 % by weight to 25 % by weight oleic acid, and 40 % by weight to 55 % by weight linoleic acid.

Friction modifiers may include fatty amines, esters such as borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxylated fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, or fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines.

In one embodiment the lubricating composition may contain phosphorus- or sulphur-containing antiwear agents other than compounds described as an extreme pressure agent of the amine salt of a phosphoric acid ester described above. Examples of the antiwear agent may include a non-ionic phosphorus compound (typically compounds having phosphorus atoms with an oxidation state of +3 or +5), a metal dialkyldithiophosphate (typically zinc dialkyldithiophosphates), a metal mono- or di- alkylphosphate (typically zinc phosphates), or mixtures thereof.

The non-ionic phosphorus compound includes a phosphite ester, a phosphate ester, or mixtures thereof.

In one embodiment the lubricating composition of the invention further includes a dispersant. The dispersant may be a succinimide dispersant (for example N-substituted long chain alkenyl succinimides), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant or a polyetheramine dispersant.

In one embodiment the succinimide dispersant includes a polyisobutylene-substituted succinimide, wherein the polyisobutylene from which the dispersant is derived may have a number average molecular weight of 400 to 5000, or 950 to 1600.

Succinimide dispersants and their methods of preparation are more fully described in U.S. Patents 4,234,435 and 3,172,892.

Suitable ester-containing dispersants are typically high molecular weight esters. These materials are described in more detail in U.S. Patent 3,381,022.

In one embodiment the dispersant includes a borated dispersant. Typically the borated dispersant includes a succinimide dispersant including a polyisobutylene succinimide, wherein the polyisobutylene from which the dispersant is derived may have a number average molecular weight of 400 to 5000. Borated dispersants are described in more detail above within the extreme pressure agent description.

Dispersant viscosity modifiers (often referred to as DVMs) include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of maleic anhydride and an amine, a polymethacrylate functionalised with an amine, or esterified styrene- maleic anhydride copolymers reacted with an amine may also be used in the composition of the invention.

Corrosion inhibitors include 1-amino-2-propanol, octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and/or a fatty acid such as oleic acid with a polyamine.

Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

Foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexyl acrylate and optionally vinyl acetate.

Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

Pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

Seal swell agents including Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

The lubricating oil composition of the presently claimed invention can be used for various applications such as light, medium and heavy duty engine oils, industrial engine oils, marine engine oils, crankshaft oils, compressor oils, refrigerator oils, hydrocarbon compressor oils, very low-temperature lubricating oils and fats, high temperature lubricating oils and fats, wire rope lubricants, textile machine oils, refrigerator oils, aviation and aerospace lubricants, aviation turbine oils, transmission oils, gas turbine oils, spindle oils, spin oils, traction fluids, transmission oils, plastic transmission oils, passenger car transmission oils, truck transmission oils, industrial transmission oils, industrial gear oils, insulating oils, instrument oils, brake fluids, transmission liquids, shock absorber oils, heat distribution medium oils, transformer oils, fats, chain oils, minimum quantity lubricants for metalworking operations, oil to the warm and cold working, oil for water-based metalworking liquids, oil for neat oil metalworking fluids, oil for semi-synthetic metalworking fluids, oil for synthetic metalworking fluids, drilling detergents for the soil exploration, hydraulic oils, in biodegradable lubricants or lubricating greases or waxes, chain saw oils, release agents, moulding fluids, gun, pistol and rifle lubricants or watch lubricants and food grade approved lubricants.

The mechanical device is preferably selected from the group consisting of bearings, gears, joints and guidances. Preferably the mechanical device is operated at temperatures in the range of ≥ 10 °C to ≤ 120 °C.

Examples

Preparation of ester compounds

Propylheptanol is commercially available from BASF SE, Ludwigshafen [93,0 % by weight 2-propyl-heptanol; 2.9 % by weight 2-propyl-4-methyl-hexanol; 3.9 % by weight 2-propyl-5-methylhexanol and 0.2 Gew.-% 2-isopropylheptanol]

DIDA is commercially available for example as Synative® ES DIDA from BASF SE, Ludwigshafen.

Preparation of Di- (2-propylheptyl)-adipate (DPHA)

A mixture of structural isomers of an alcohol with 10 carbon atoms which is available by BASF SE as "propylheptanol" (2.4 mol) and adipic acid (1.0 mol) is reacted in the present of iso-propyl-butyl-titanate (0.001 mol) in an autoclave under inert gas (N_2) at a reaction temperature of 230°C. Water which is formed during the reaction is removed from the reaction mixture through an inert gas stream (N_2-stream). After 180 minutes the excess alcohol is removed from the mixture by distillation at a pressure of 50 mbar. The thus obtained adipic acid ester is then neutralised with 0.5% NaOH at 80 °C. Afterwards the organic phase and the aqueous phase are separated, followed by washing the organic phase two times with water. In a further step the organic phase is purified by treating the crude adipic acid ester with steam at 180°C and 50 mbar. Then the ester is dried by subjecting it to a N_2 stream at 150°C and 50 mbar. Finally the ester is mixed with activated carbon and is filtered using as a rheological agent supra-theorit at 80°C under reduced pressure. The adipic acid ester shows a density of 0.916g/cm^3 at 20°C, measured according to DIN 51757, respectively ASTM D 4052.

Preparation of lubricant formulations

Table 1: Lubricant formulations A and B (all values in weight-%)

	Formulation A with DIDA	Formulation B with DPHA
PAO 6 (Nexbase® 2006, polyalphaolefin, obtainable from Neste Oil N.V, Belgium)	52.0 %	52.0 %
DIDA	10.0 %	-
DPHA	-	10.0 %
Thickener (Lubrizol® 8406, polyisobutylene, available from Lubrizol)	13.0 %	13.0 %
Thickener (Lubrizol® 8407 from Lubrizol)	13.0 %	13.0%
Additives (Anglamol® 6004, additive package available from Lubrizol)	12.0 %	12.0 %

Friction coefficient evaluation

The fluids were tested in the MTM (Mini-Traction Machine) instrument using the so-called traction test mode. In this mode, the friction coefficient is measured at a constant mean speed over a range of slide roll ratios (SRR) to give the traction curve. SRR = sliding speed /mean entrainment speed = 2 (U1-U2)/(U1+U2) in which U1 and U2 are the ball and disc speeds respectively

The disc and ball used for the experiments were made of steel (AISI 52100), with a hardness of 750 HV and Ra < 0,02 µm. The diameter was 45,0 mm and 19,0 mm for the disc and the ball respectively. The tractions curves were run with 1,00 GPa contact pressure, 10 to 1000 m/s speed and different temperatures such as 40 °C and 100 °C. The slide-roll ratio (SRR) was 50 % and the friction coefficient measured. Each sample (20 ml) was run three times.

Results of the evaluation

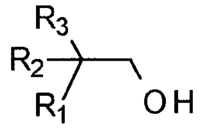
The results of the MTM testing are shown in Figures 1 and 2. In each case the upper curve is obtained from evaluation of Formulation A and the lower curve is obtained from evaluation of Formulation B. Figure 1 refers to the results when testing was carried out at 40 °C, whereas Figure 2 refers to the results to the results when testing was carried out at 100 °C.

In each case the formulations containing esters according to the presently claimed invention show a significantly lower coefficient of friction.

Claims:

1. A method for reducing the friction coefficient of a lubricating oil composition in the lubrication of a mechanical device

   comprising formulating said lubricating oil composition with a carboxylic acid ester obtainable by reacting a mixture comprising
   a) at least one dicarboxylic acid, optionally in form of its anhydride, and
   b1) at least one monoalcohol having 10 carbon atoms and a structure of general formula I,



I,

   wherein R^1 is pentyl, R^2 is H and R^3 is propyl.

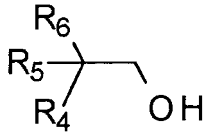
2. The method according to claim 1, wherein the friction coefficient is measured at 25% slide roll ratio (SRR) using mini-traction machine (MTM) measurements at 70 °C and 1 GPa.

3. The method according to claim 1 or 2, wherein the dicarboxylic acid is selected from the group consisting of phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, glutaric acid, diglycolic acid, 1,4-cyclohexanedicarboxylic acid, 2,6-decahydronaphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid and 2,5-norbornanedicarboxylic acid.

4. The method according to one or more of claims 1 to 3, wherein the dicarboxylic acid is selected from the group consisting of glutaric acid, diglycolic acid, succinic acid, azelaic acid, sebacic acid, 1,4-cyclohexanedicarboxylic acid, adipic acid, 2,6-decahydronaphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid and 2,5-norbornanedicarboxylic acid.

5. The method according to one or more of claims 1 to 4, wherein the dicarboxylic acid is adipic acid.

6. The method according to claim 1, wherein the mixture further comprises a monoalcohol b2) having 10 carbon atoms and a structure of the general formula II,



II,

   wherein

   R_4 is selected from the group consisting of pentyl, iso-pentyl, 2-methyl-butyl, 3-methyl-butyl and 2,2-dimethyl-propyl,

R_5 is H or methyl and

R_6 is selected from the group consisting of ethyl, propyl and iso-propyl,

whereby the monoalcohol b1) and the monoalcohol b2) have a different structure.

7. The method according to one or more of claims 1 to 6, wherein weight ratio of monoalcohol b1) to monoalcohol b2) is in the range of 5:1 to 95:1.

8. The method according to one or more of claims 1 to 7, wherein the monoalcohol b1) is present in a molar ratio in the range of 2.05:1 to 3.0:1 in relation to the acid a).

9. The method according to one or more of claims 1 to 8, wherein the lubricating oil composition comprises ≥ 1 % to ≤ 10 % by weight or ≥ 1 % to ≤ 40 % by weight or ≥ 20 % to ≤ 100 % by weight of at least one carboxylic acid ester, related to the total amount of the lubricating oil composition.

10. The method according to one or more of claims 1 to 9, wherein the lubricating oil composition further comprises base stocks selected from the group consisting of mineral oils (Gr I, II or III oils), polyalphaolefins, polymerized and interpolymerized olefins, alkyl naphthalenes, alkylene oxide polymers, silicone oils and phosphate esters.

11. The method according to claim 10, wherein the lubricating oil comprises ≥ 1 % to ≤ 49 % by weight or ≥ 50 % to ≤ 99 % by weight base stocks, related to the total amount of the lubricating oil composition.

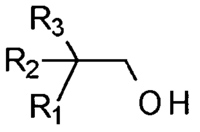
12. The method according to one or more of claims 1 to 11, wherein the mechanical device is selected from the group consisting of bearings, actuator, gears, piston, cranked shaft, joints and guidances.

13. The method according to one or more of claims 1 to 12, wherein the mechanical device is operated at temperatures in the range of ≥ 10 °C to ≤ 120 °C.

14. The use of a carboxylic acid ester obtainable by reacting a mixture comprising

   a) at least one dicarboxylic acid, optionally in form of its anhydride, and

   b1) at least one monoalcohol having 10 carbon atoms and a structure of general formula I,

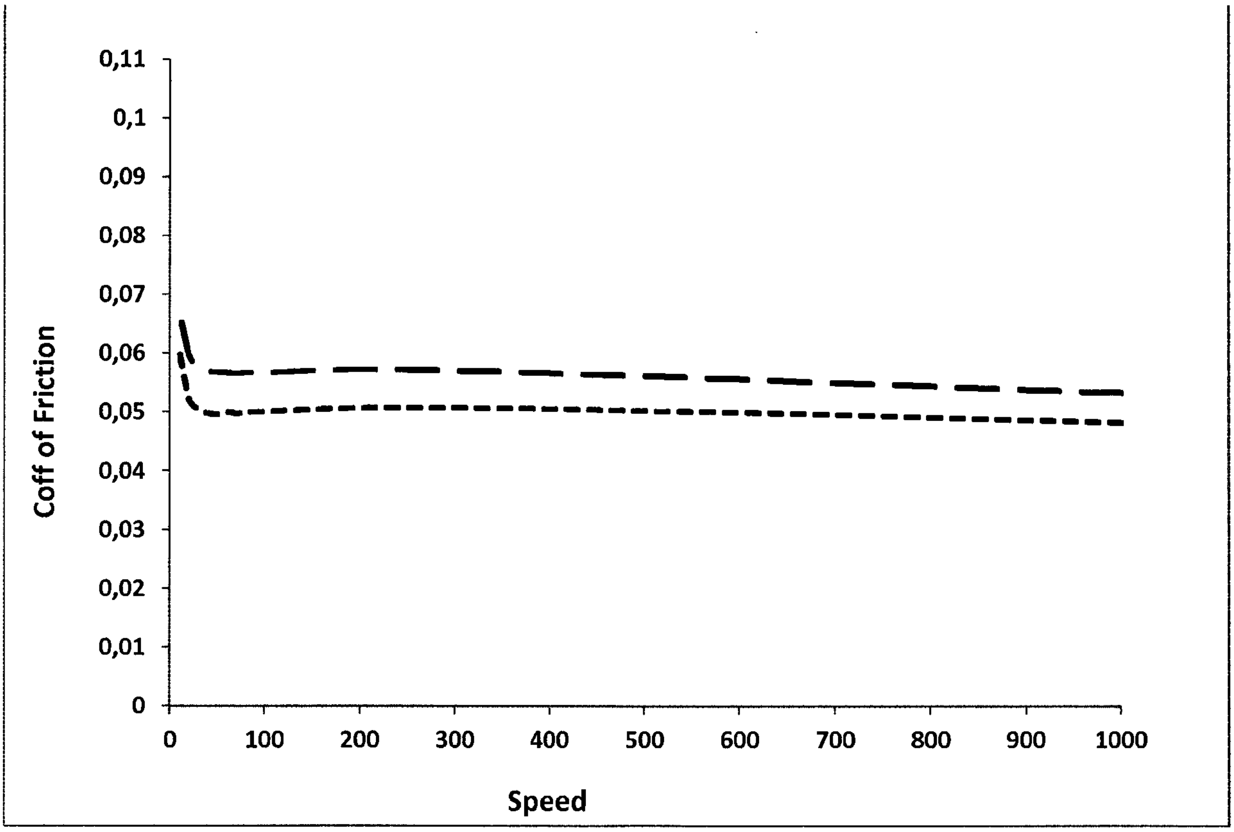


I,

wherein R^1 is pentyl, R^2 is H and R^3 is propyl, for reducing the friction coefficient of a lubricating oil composition in the lubrication of a mechanical device.

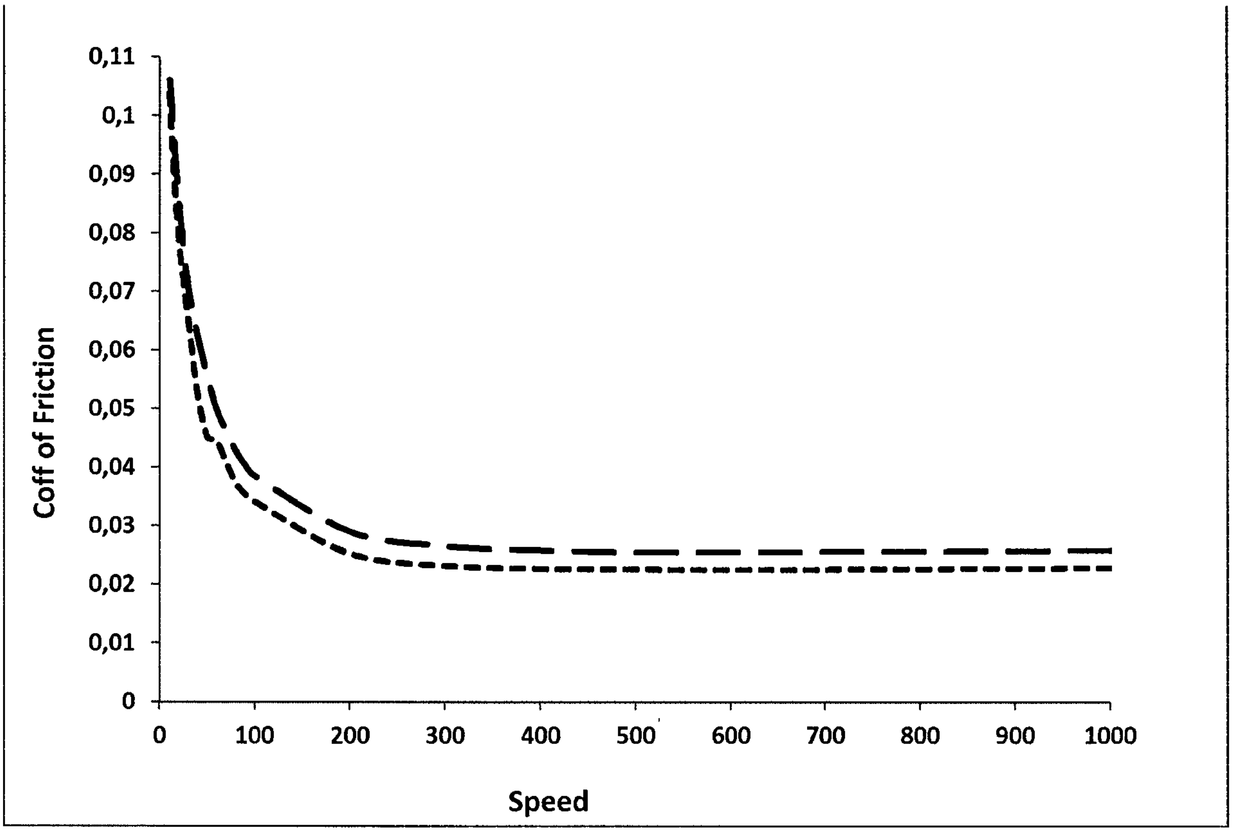
15. The use according to claim 14, wherein the friction coefficient is measured at 25% slide roll ratio (SRR) using mini-traction machine (MTM) measurements at 70 °C and 1 GPa.

Figure 1


0,11
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
Coff of Friction
0
100
200
300
400
500
600
700
800
900
1000
Speed

5

Figure 2


Coff of Friction
0,11
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
0
100
200
300
400
500
600
700
800
900
1000
Speed

5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/059338

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M105/36 C10M129/72
ADD. C10N30/06 C10N40/02 C10N40/04 C10N40/25

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C10N

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/261628 A1 (SCHERER MARKUS [DE] ET AL) 14 October 2010 (2010-10-14) paragraphs [0011], [0046]; claims 17,20,24 -----	1-15
X	US 2 921 089 A (HAGEMEYER JR HUGH J ET AL) 12 January 1960 (1960-01-12) column 2, lines 40-41; claim 1 -----	1,3-5,8, 9,14
X	US 2012/202725 A1 (GRASS MICHAEL [DE] ET AL) 9 August 2012 (2012-08-09) paragraphs [0012], [0095] - [0096]; claims 1,15; example 2 -----	1,6-9,14
X	DE 102 01 348 A1 (OXENO OLEFINCHEMIE GMBH [DE]) 24 April 2003 (2003-04-24) paragraph [0062]; example 5 ----- -/--	1,3-6,8, 9,14

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 8 July 2014	Date of mailing of the international search report 21/07/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bertrand, Samuel

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/059338

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/093579 A1 (BOYDE STEPHEN [GB] ET AL) 15 April 2010 (2010-04-15) claim 6; tables 1-2 -----	1-15
A	US 2012/208731 A1 (LANN PAMELA [US] ET AL) 16 August 2012 (2012-08-16) cited in the application paragraph [0001]; claim 1 -----	1-15

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/059338

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010261628 A1	14-10-2010	CA 2637401 A1	26-07-2007
		DE 102006001768 A1	19-07-2007
		EP 1973999 A1	01-10-2008
		JP 5412116 B2	12-02-2014
		JP 2009523182 A	18-06-2009
		US 2010261628 A1	14-10-2010
		US 2013137614 A1	30-05-2013
		WO 2007082639 A1	26-07-2007
US 2921089 A	12-01-1960	FR 1231677 A	30-09-1960
		GB 893763 A	11-04-1962
		US 2921089 A	12-01-1960
US 2012202725 A1	09-08-2012	CN 102596928 A	18-07-2012
		DE 102009028976 A1	03-03-2011
		EP 2470517 A1	04-07-2012
		JP 2013503120 A	31-01-2013
		KR 20120066644 A	22-06-2012
		US 2012202725 A1	09-08-2012
		WO 2011023491 A1	03-03-2011
DE 10201348 A1	24-04-2003	DE 10201348 A1	24-04-2003
		ES 2302836 T3	01-08-2008
		JP 2009007353 A	15-01-2009
		KR 20040037128 A	04-05-2004
		ZA 200403114 A	28-01-2005
US 2010093579 A1	15-04-2010	EP 2118246 A2	18-11-2009
		JP 2010520319 A	10-06-2010
		US 2010093579 A1	15-04-2010
		WO 2008104745 A2	04-09-2008
US 2012208731 A1	16-08-2012	AU 2010295801 A1	05-04-2012
		CA 2774273 A1	24-03-2011
		CN 102597190 A	18-07-2012
		EP 2478079 A1	25-07-2012
		JP 2013505329 A	14-02-2013
		KR 20120093211 A	22-08-2012
		US 2012208731 A1	16-08-2012
		WO 2011034829 A1	24-03-2011

(19) 中华人民共和国国家知识产权局

(12) 发明专利申请

(10) 申请公布号 CN 105229125 A
(43) 申请公布日 2016.01.06

(21) 申请号 201480026817.4

(22) 申请日 2014.05.07

(30) 优先权数据
13167627.2 2013.05.14 EP
13181269.5 2013.08.22 EP

(85) PCT国际申请进入国家阶段日
2015.11.11

(86) PCT国际申请的申请数据
PCT/EP2014/059338 2014.05.07

(87) PCT国际申请的公布数据
WO2014/184068 EN 2014.11.20

(71) 申请人 巴斯夫欧洲公司
地址 德国路德维希港

(72) 发明人 M·舍尔　A·戈亚尔　M·艾科米尔
B·布莱特沙伊德

(74) 专利代理机构 北京市中咨律师事务所 11247
代理人 王丹丹　刘金辉

(51) Int.Cl.
C10M 105/36(2006.01)
C10M 129/72(2006.01)
C10N 30/06(2006.01)
C10N 40/02(2006.01)
C10N 40/04(2006.01)
C10N 40/25(2006.01)

权利要求书2页　说明书10页　附图1页

(54) 发明名称

具有增强能量效率的润滑油组合物

(57) 摘要

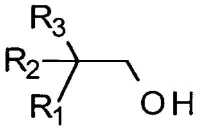
本发明涉及在机械装置的润滑中降低润滑油组合物的摩擦系数的方法，其包括用可通过使包含至少一种二羧酸和至少一种支化C_{10}醇的混合物反应而得到的羧酸酯配制所述润滑油组合物。

1. 在机械装置的润滑中降低润滑油组合物的摩擦系数的方法，其包括：

用可通过使包含以下组分的混合物反应而得到的羧酸酯配制所述润滑油组合物：

a) 至少一种二羧酸，任选为其酐的形式，和

b1) 至少一种具有10个碳原子和通式I结构的单醇：



I

其中R^1为戊基，R^2为H且R^3为丙基。

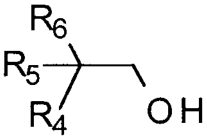
2. 根据权利要求1的方法，其中摩擦系数在70℃和1GPa下使用微牵引力测定仪(MTM)测量以25%滑滚比(SRR)测量。

3. 根据权利要求1或2的方法，其中二羧酸选自邻苯二甲酸、琥珀酸、烷基琥珀酸、烯基琥珀酸、马来酸、壬二酸、辛二酸、癸二酸、富马酸、己二酸、亚油酸二聚物、丙二酸、烷基丙二酸、烯基丙二酸、戊二酸、二甘醇酸、1,4-环己烷二羧酸、2,6-十氢化萘二羧酸、1,3-环己烷二羧酸和2,5-降莰烷二羧酸。

4. 根据权利要求1-3中任一项的方法，其中二羧酸选自戊二酸、二甘醇酸、琥珀酸、壬二酸、癸二酸、1,4-环己烷二羧酸、己二酸、2,6-十氢化萘二羧酸、1,3-环己烷二羧酸和2,5-降莰烷二羧酸。

5. 根据权利要求1-4中任一项的方法，其中二羧酸为己二酸。

6. 根据权利要求1的方法，其中混合物进一步包含具有10个碳原子和通式II结构的单醇b2)：



II

其中：

R_4选自戊基、异戊基、2-甲基-丁基、3-甲基-丁基和2,2-二甲基-丙基，

R_5为H或甲基，且

R_6选自乙基、丙基和异丙基，

其中单醇b1)和单醇b2)具有不同的结构。

7. 根据权利要求1-6中任一项的方法，其中单醇b1)与单醇b2)的重量比为5:1-95:1。

8. 根据权利要求1-7中任一项的方法，其中单醇b1)以相对于酸a)为2.05:1-3.0:1的摩尔比存在。

9. 根据权利要求1-8中任一项的方法，其中润滑油组合物包含相对于润滑油组合物的总量≥1%至≤10重量%或者≥1%至≤40重量%或者≥20%至≤100重量%的至少一种羧酸酯。

10. 根据权利要求1-9中任一项的方法，其中润滑油组合物进一步包含选自矿物油(第

I、II 或 III 组油）、聚α烯烃、聚合和共聚烯烃、烷基萘、氧化烯聚合物、硅油和磷酸酯的基本油料。

11. 根据权利要求 10 的方法，其中润滑油包含相对于润滑油组合物的总量≥ 1%至≤ 49 重量%或者≥ 50%至≤ 99 重量%基本油料。

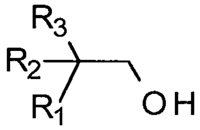
12. 根据权利要求 1-11 中任一项的方法，其中机械装置选自轴承、促动器、齿轮、活塞、曲柄轴、接头和导航。

13. 根据权利要求 1-12 中任一项的方法，其中机械装置在≥ 10℃至≤ 120℃的温度下操作。

14. 可通过使包含以下组分的混合物反应而得到的羧酸酯在机械装置的润滑中降低润滑油组合物摩擦系数的用途：

a) 至少一种二羧酸，任选为其酐的形式，和

b1) 至少一种具有 10 个碳原子和通式 I 结构的单醇：



I

其中 R^1为戊基，R^2为 H 且 R^3为丙基。

15. 根据权利要求 14 的用途，其中摩擦系数在 70℃和 1GPa 下使用微牵引力测定仪 (MTM) 测量以 25%滑滚比 (SRR) 测量。

具有增强能量效率的润滑油组合物

[0001]　本发明涉及在机械装置的润滑中降低润滑油组合物的摩擦系数的方法，其包括用可通过使包含至少一种二羧酸和至少一种支化 C_{10}醇的混合物反应而得到的羧酸酯配制所述润滑油组合物。

[0002]　市售润滑油组合物由多种不同的天然或合成组分制备。为改进所需性能，根据使用领域，通常加入其它添加剂。基油通常由矿物油、高精炼矿物油、烷基化矿物油、聚－α－烯烃（PAO）、聚亚烷基二醇、磷酸酯、硅油、二酯和多元醇酯组成。

[0003]　不同的润滑剂，例如发动机油、涡轮机油、液压流体、变速器用油、压缩机油等必须满足极高的标准，例如高粘度指数、良好的润滑剂性能、高氧化稳定性、良好的热稳定性或相当的性能。

[0004]　用作变速器、工业或发动机油的高性能润滑油配制剂为具有在剪切稳定性、低温粘度、长使用寿命、蒸发损失、燃料效率、密封相容性和磨损保护方面的特殊性能特征的油。除常规添加剂组分外，这类油目前优选用 PAO（尤其是 PAO 6）或者第 I、II 或 III 组矿物油作为载液，并且用特殊聚合物（聚异丁烯＝PIB，烯烃共聚物＝乙烯／丙烯共聚物＝OCP，聚甲基丙烯酸烷基酯＝PMA）作为增稠剂或粘度指数改进剂配制。与 PAO 一起，低粘度酯通常使用例如 DIDA（己二酸二异癸酯）、DITA（己二酸二－异十三烷基酯）或 TMTC（三羟甲基丙烷辛酸酯），尤其是作为极性添加剂类型的增溶剂和用于使密封相容性最佳化。

[0005]　酯作为助溶剂尤其用于发动机油、涡轮机油、液压流体、变速器用油、压缩机油，但酯也用作基油，其中它们为主要组分。

[0006]　EP 0 767 236 A1 公开了一种齿轮润滑油组合物。该组合物含有大于 20 体积％氢化聚 α－烯烃和小于 80 体积％矿物油或合成酯油或其组合。实例含有 10 体积％己二酸双（十三烷基）酯。

[0007]　WO 98/04658 A1 公开了用于重型和中型车轴齿轮润滑剂和传动流体应用中的合成齿轮油用基本油料。此处公开的润滑剂含有 1-20 重量％酯。该酯包括 C_{8-13}己二酸酯的二酯，特别是己二酸二－异癸酯。

[0008]　美国专利 4,370,247 公开了含有 25-60 质量％至少一种二羧酸的二 -C_{8-12}烷基酯的齿轮或车轴润滑剂。报告了此处公开的整个润滑剂降低了由于摩擦导致的功率损耗，因此保持燃料消耗。

[0009]　CA 2 637 401 公开了衍生自具有 2-36 个碳原子的二羧酸和具有 4-40 个碳原子的支化醇的多种二酯。该润滑剂可含有 0.1-100 重量％或 5-99 重量％二酯。

[0010]　WO 2011/34829 A1 公开了润滑限滑差速器的方法，其包括向限滑差速器中供入包含己二酸的 C_{4-30}二酯的润滑组合物。

[0011]　尽管不同的润滑剂，例如发动机油、涡轮机油、液压流体、变速器用油、压缩机油等满足极高的标准，例如高粘度指数、良好的润滑剂性能、高氧化稳定性和良好热稳定性，仍需要降低机械装置操作期间消耗的能量。

[0012]　因此，本发明的目的是提供容许以较低的能量消耗操作机械装置的方法。

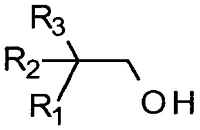
[0013]　该目的通过提供在机械装置的润滑中降低润滑油组合物的摩擦系数的方法而实

现，所述方法包括用可通过使包含以下组分的混合物反应而得到的羧酸酯配制所述润滑油组合物：

[0014]　a) 至少一种二羧酸，任选为其酐的形式，和

[0015]　b1) 至少一种具有 10 个碳原子和通式 I 结构的单醇：

[0016]



I

[0017]　其中 R^1为戊基，R^2为 H 且 R^3为丙基。

[0018]　在本发明意义上，术语润滑油组合物意指能够降低移动表面之间的摩擦的物质。

[0019]　摩擦改进性能通过使用微牵引力测定仪 (MTM) 测量在 70℃和 1GPa 下以 25％滑滚比 (SRR) 测量摩擦系数而测定。

[0020]　在本发明意义上，降低摩擦系数意指包含如上所述羧酸酯的润滑油组合物的摩擦系数低于不包含所述羧酸酯的润滑油组合物的摩擦系数。

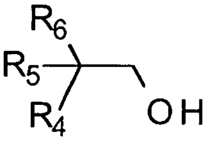
[0021]　在本发明意义上，机械装置为由基于机械原理工作的装置组成的机制。

[0022]　优选，二羧酸选自邻苯二甲酸、琥珀酸、烷基琥珀酸和烯基琥珀酸、马来酸、壬二酸、辛二酸、癸二酸、富马酸、己二酸、亚油酸二聚物、丙二酸、烷基丙二酸、烯基丙二酸、戊二酸、二甘醇酸、1,4- 环己烷二羧酸、2,6- 十氢化萘二羧酸、1,3- 环己烷二羧酸和 2,5- 降莰烷二羧酸。更优选，二羧酸选自戊二酸、二甘醇酸、琥珀酸、壬二酸、癸二酸、1,4- 环己烷二羧酸、己二酸、2,6- 十氢化萘二羧酸、1,3- 环己烷二羧酸和 2,5- 降莰烷二羧酸。最优选，脂族二羧酸为己二酸。

[0023]　二羧酸可以以纯形式或者以与单羧酸的混合物的形式使用。代替二羧酸，也可使用它们的酐。代表性单羧酸包括正丁酸、正戊酸、正己酸、正庚酸、正辛酸、正壬酸、正癸酸、异丁酸、异戊酸、异己酸、异庚酸、异辛酸、2- 乙基己酸、异壬酸、3,5,5- 三甲基己酸和异癸酸。

[0024]　优选，混合物进一步包含具有 10 个碳原子和通式 II 结构的单醇 b2)：

[0025]



II

[0026]　其中：

[0027]　R_4选自戊基、异戊基、2- 甲基 - 丁基、3- 甲基 - 丁基和 2,2- 二甲基 - 丙基，

[0028]　R_5为 H 或甲基，且

[0029]　R_6选自乙基、丙基和异丙基，

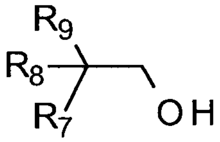
[0030]　其中单醇 b1) 和单醇 b2) 具有不同的结构。

[0031] 优选，单醇 b2) 选自 2- 丙基 -4- 甲基 - 己醇、2- 丙基 -5- 甲基 - 己醇、2- 异丙基 -4- 甲基 - 己醇、2- 异丙基 -5- 甲基 - 己醇、2- 丙基 -4,4- 二甲基戊醇、2- 乙基 -2,4- 二甲基己醇、2- 乙基 -2- 甲基 - 庚醇、2- 乙基 -2,5- 二甲基己醇和 2- 异丙基 - 庚醇。更优选，单醇 b2) 为 2- 丙基 -4- 甲基 - 己醇。

[0032] 优选，单醇 b1) 与单醇 b2) 的重量比为 5:1-95:1，更优选 6:1-50:1，甚至更优选 10:1-40:1，最优选 20:1-35:1。

[0033] 优选，混合物进一步包含具有 10 个碳原子和通式 III 结构的单醇 b3)：

[0034]



III

[0035] 其中：

[0036] R_7选自戊基、异戊基、2- 甲基 - 丁基、3- 甲基 - 丁基和 2,2- 二甲基 - 丙基，

[0037] R_8为 H 或甲基，

[0038] R_9选自乙基、丙基和异丙基。

[0039] 优选，单醇 b3) 具有与单醇 b1) 和单醇 b2) 不同的结构。优选，单醇 b3) 选自 2- 丙基 -5- 甲基 - 己醇、2- 异丙基 -4- 甲基 - 己醇、2- 异丙基 -5- 甲基 - 己醇、2- 丙基 -4,4- 二甲基戊醇、2- 乙基 -2,4- 二甲基己醇、2- 乙基 -2- 甲基 - 庚醇、2- 乙基 -2,5- 二甲基己醇和 2- 异丙基 - 庚醇。更优选，单醇 b3) 为 2- 丙基 -5- 甲基 - 己醇。

[0040] 优选，混合物包含 80-95 重量％ 2- 正丙基 - 庚醇作为组分 b1)，1.0-10 重量％ 2- 丙基 -4- 甲基 - 己醇作为组分 b2)，1.0-10 重量％ 2- 丙基 -5- 甲基 - 己醇作为组分 b3) 和 0.1-2.0 重量％ 2- 异丙基 - 庚醇，其中各组分的重量涉及单醇的总重量。更优选，混合物包含 91.0-95.0 重量％ 2- 正丙基 - 庚醇作为组分 b1)，2.0-5.0 重量％ 2- 丙基 -4- 甲基 - 己醇作为组分 b2)，3.0-5.0 重量％ 2- 丙基 -5- 甲基 - 己醇作为组分 b3) 和 0.1-0.8 重量％ 2- 异丙基 - 庚醇，其中各组分的重量涉及单醇的总重量。

[0041] 优选，单醇 b1) 以相对于酸 a) 为 2.05:1-3.0:1，更优选 2.1:1-2.5:1 的摩尔比存在。

[0042] 优选，润滑油组合物包含相对于润滑油组合物的总量≥ 1％至≤ 10 重量％或者≥ 1％至≤ 40 重量％或者≥ 20％至≤ 100 重量％，更优选≥ 1％至≤ 5 重量％或者≥ 1％至≤ 35 重量％或者≥ 25％至≤ 100 重量％，最优选≥ 1％至≤ 2 重量％或者≥ 2％至≤ 30 重量％或者≥ 30％至≤ 100 重量％的至少一种如上文所定义的羧酸酯。

[0043] 优选，润滑油组合物进一步包含选自矿物油（第 I、II 或 III 组油）、聚 α 烯烃、聚合和共聚烯烃、烷基萘、氧化烯聚合物、硅油、磷酸酯和羧酸酯的其它基本油料。优选，润滑油包含相对于润滑油组合物的总量≥ 50％至≤ 99 重量％或者≥ 80％至≤ 99 重量％或者≥ 90％至≤ 99 重量％基本油料。

[0044] 本发明中关于基本油料的定义与 American Petroleum Institute(API) 出版物 “Engine Oil Licensing and Certification System”，Industry Services Department，

第14版，1996年12月，附录1，1998年12月中找到的那些相同。所述出版物将基本油料如下分类：

[0045] a）使用下表所述试验方法，第I组基本油料包含小于90％饱和物和／或大于0.03％硫，且具有大于或等于80且小于120的粘度指数，

[0046] b）使用下表所述试验方法，第II组基本油料包含大于或等于90％饱和物和小于或等于0.03％硫，且具有大于或等于80且小于120的粘度指数，

[0047] c）使用下表所述试验方法，第III组基本油料包含大于或等于90％饱和物和小于或等于0.03％硫，且具有大于或等于120的粘度指数。

[0048] 基本油料的分析方法

[0049]

性能	测试方法
饱和物	ASTM D 2007
粘度指数	ASTM D 2270
硫	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

[0050] 适于本发明的合成较低粘度流体包括聚α烯烃（PAO）以及来自费托高沸点馏分，包括蜡的加氢裂化或加氢异构化的合成油。这些为包含与其合成来源一致具有低杂质含量的饱和物的原料。加氢异构化费托合成蜡为非常合适的基本油料，其包含具有异链烷烃性质的饱和组分（由费托合成蜡的主要正链烷烃的异构化产生），这赋予高粘度指数和低倾点的良好混合。费托合成蜡的加氢异构化方法描述于美国专利5,362,378；5,565,086；5,246,566和5,135,638以及EP 710710、EP 321302和EP 321304中。

[0051] 适于本发明的聚α烯烃取决于其具体性能作为较低粘度或高粘度流体包括已知的PAO材料，其通常包含α烯烃的较低分子量氢化聚合物或低聚物，所述α烯烃包括但不限于C_2至约C_{32}α烯烃，其中优选C_8至约C_{16}α烯烃，例如1-辛烯、1-癸烯、1-十二碳烯等。优选的聚α烯烃为聚-1-辛烯、聚-1-癸烯和聚-1-十二碳烯，但C_{14}-C_{18}范围内的较高烯烃的二聚物提供低粘度基本油料。

[0052] 适于本发明的低粘度PAO流体可方便地通过α烯烃在聚合催化剂如Friedel-Crafts催化剂，包括例如三氯化铝、三氟化硼或者三氟化硼与水、醇如乙醇、丙醇或丁醇、羧酸或酯如乙酸乙酯或丙酸乙酯的络合物的存在下聚合而制备。例如，美国专利4,149,178或3,382,291公开的方法可方便地用于本文中。关于PAO合成的其它描述在以下美国专利中找到：3,742,082(Brennan)；3,769,363(Brennan)；3,876,720(Heilman)；4,239,930(Allphin)；4,367,352(Watts)；4,413,156(Watts)；4,434,408(Larkin)；4,910,355(Shubkin)；4,956,122(Watts)；和5,068,487(Theriot)。

[0053]　合成润滑油包括烃油和卤素取代烃油，例如聚合和共聚烯烃（例如聚丁烯、聚丙烯、丙烯－异丁烯共聚物、氯化聚丁烯、聚（1-己烯）、聚（1-辛烯）、聚（1-癸烯））；烷基苯（例如十二烷基苯、十四烷基苯、二壬基苯、二（2-乙基己基）苯）；聚苯（例如联苯、三联苯、烷基化多酚）；和烷基化二苯醚和烷基化二苯硫醚及其衍生物、类似物和同系物。

[0054]　适于本发明的其它羧酸酯包括单和多元酸与单醇（简单酯）或者与单和多元醇的混合物（混合酯）的酯，以及单羧酸（简单酯）或者单和聚羧酸的混合物（混合酯）的多元醇酯。一元／多元类型的酯可包括例如单羧酸如庚酸和二羧酸如邻苯二甲酸、琥珀酸、烷基琥珀酸、烯基琥珀酸、马来酸、壬二酸、辛二酸、癸二酸、富马酸、己二酸、亚油酸二聚物、丙二酸、烷基丙二酸、烯基丙二酸等与多种醇如丁醇、己醇、十二醇、2-乙基己醇或其与多元醇的混合物的酯。这些类型的酯的具体实例包括庚酸壬酯、己二酸二丁酯、癸二酸二（2-乙基己基）酯、富马酸二－己基酯、癸二酸二辛酯、壬二酸二异辛酯、壬二酸二异癸酯、邻苯二甲酸二辛酯、邻苯二甲酸二癸酯、癸二酸二－二十烷基酯、TMP-己二酸二丁酯等。

[0055]　适于本发明的还有酯，例如通过使一种或多种多元醇，优选受阻多元醇，例如新戊基多元醇如新戊二醇、三羟甲基乙烷、2-甲基-2-丙基-1,3-丙二醇、三羟甲基丙烷、三羟甲基丁烷、季戊四醇和二季戊四醇与包含至少4个碳的单羧酸，通常C_5-C_{30}酸如饱和直链脂肪酸，包括辛酸、癸酸、月桂酸、肉豆蔻酸、棕榈酸、硬脂酸、花生酸和山萮酸，或者相应的支链脂肪酸或不饱和脂肪酸如油酸或其混合物与聚羧酸反应而得到的那些。

[0056]　其中末端羟基通过酯化、醚化等改性的氧化烯聚合物和共聚物及其衍生物构成另一类已知的合成润滑油。这些通过如下例证：通过氧化乙烯或氧化丙烯聚合制备的聚氧化烯聚合物，和聚氧化烯聚合物的烷基和芳基醚（例如分子量为1000的甲基－聚异丙二醇醚或分子量为1000-1500的聚乙二醇二苯基醚）；及其单－和多羧酸酯，例如四甘醇的乙酸酯、混合C_3-C_8脂肪酸酯和C_{13}含氧酸二酯。

[0057]　硅基油如聚烷基－、聚芳基－、聚烷氧基－或聚芳氧基硅油和硅酸酯油包括另一类有用的合成润滑剂；这种油包括硅酸四乙酯、硅酸四异丙酯、硅酸四-(2-乙基己基）酯、硅酸四-(4-甲基-2-乙基己基）酯、硅酸四-(对－叔丁基－苯基）酯、六-(4-甲基-2-乙基己基）二硅氧烷、聚（甲基）硅氧烷和聚（甲基苯基）硅氧烷。其它合成润滑油包括含磷酸的液体酯（例如磷酸三甲苯酯、磷酸三辛基酯、癸基膦酸的二乙基酯）和聚四氢呋喃。

[0058]　本发明润滑油组合物任选进一步包含至少一种其它性能添加剂。其它性能添加剂包括分散剂、金属减活剂、清净剂、粘度改进剂、极压剂（通常含硼和／或含硫和／或含磷）、抗磨剂、抗氧化剂（例如受阻酚、胺类抗氧化剂或钼化合物）、腐蚀抑制剂、抑泡剂、反乳化剂、倾点下降剂、密封溶胀剂、摩擦改进剂及其混合物。

[0059]　存在的其它性能添加剂（不包括粘度改进剂）的总组合量基于无油可包括组合物的0重量％至25重量％，或者0.01重量％至20重量％，或者0.1重量％至15重量％或0.5重量％至10重量％，或者1-5重量％的范围。

[0060]　尽管可存在一种或多种其它性能添加剂，通常其它性能添加剂以相对于彼此不同的量存在。

[0061]　在一个实施方案中，润滑组合物进一步包含一种或多种粘度改进剂。

[0062]　当存在时，粘度改进剂可以以润滑组合物的0.5重量％至70重量％、1重量％至60重量％，或者5重量％至50重量％，或者10重量％至50重量％的量存在。

[0063] 粘度改进剂包括：(a) 聚甲基丙烯酸酯，(b)(i) 乙烯基芳族单体和 (ii) 不饱和羧酸、酐或其衍生物的酯化共聚物，(c)(i) α－烯烃；和 (ii) 不饱和羧酸、酐或其衍生物的酯化共聚体，或者 (d) 苯乙烯－丁二烯的氢化共聚物，(e) 乙烯－丙烯共聚物，(f) 聚异丁烯，(g) 氢化苯乙烯－异戊二烯聚合物，(h) 氢化异戊二烯聚合物，或者 (i) 其混合物。

[0064] 在一个实施方案中，粘度改进剂包括：(a) 聚甲基丙烯酸酯，(b)(i) 乙烯基芳族单体；和 (ii) 不饱和羧酸、酐或其衍生物的酯化共聚物，(c)(i) α－烯烃；和 (ii) 不饱和羧酸、酐或其衍生物的酯化共聚体，或者 (d) 其混合物。

[0065] 极压剂包括含有硼和／或硫和／或磷的化合物。

[0066] 极压剂可以以润滑组合物的 0 重量％至 20 重量％，或者 0.05 重量％至 10 重量％，或者 0.1 重量％至 8 重量％存在于润滑组合物中。

[0067] 在一个实施方案中，极压剂为含硫化合物。在一个实施方案中，含硫化合物可以为硫化烯烃、多硫化物或其混合物。硫化烯烃的实例包括衍生自丙烯、异丁烯、戊烯的硫化烯烃；有机硫化物和／或多硫化物，包括苄基二硫；双－(氯苄基)二硫；二丁基四硫；二－叔丁基多硫化物；和硫化油酸甲酯、硫化烷基苯酚、硫化二戊烯、硫化萜烯、硫化迪尔斯阿尔德加合物、烷基磺苯基 N'N- 二烷基二硫代氨基酸酯；或其混合物。

[0068] 在一个实施方案中，硫化烯烃包括衍生自丙烯、异丁烯、戊烯的硫化烯烃或其混合物。

[0069] 在一个实施方案中，极压剂含硫化合物包括二巯基噻二唑或者其衍生物或混合物。二巯基噻二唑的实例包括化合物，例如 2,5- 二巯基 -1,3,4- 噻二唑或烃基取代 2,5- 二巯基 -1,3,4- 噻二唑，或者其低聚物。烃基取代 2,5- 二巯基 -1,3,4- 噻二唑的低聚物通常通过在 2,5- 二巯基 -1,3,4- 噻二唑单元之间形成硫－硫键以形成具有两个或更多个所述噻二唑单元的衍生物或低聚物而形成。合适的 2,5- 二巯基 -1,3,4- 噻二唑衍生化合物包括例如 2,5- 双(叔壬基二硫代)-1,3,4- 噻二唑或 2- 叔壬基二硫代 -5- 巯基 -1,3,4- 噻二唑。烃基取代 2,5- 二巯基 -1,3,4- 噻二唑的烃基取代基上的碳原子数目通常包括 1-30，或者 2-20，或者 3-16。

[0070] 在一个实施方案中，二巯基噻二唑可以为噻二唑－官能化分散剂。关于噻二唑－官能化分散剂的详细描述为国际公开 WO 2008/014315 的第 [0028] 至 [0052] 段。

[0071] 噻二唑官能化分散剂可通过一种方法制备，所述方法包括将噻二唑化合物与分散剂基质加热、反应或络合。可将噻二唑化合物与分散剂或其混合物共价结合、盐化、络合或者溶解。

[0072] 用于制备噻二唑官能化分散剂的分散剂基质和噻二唑的相对量可改变。在一个实施方案中，噻二唑化合物相对于 100 重量份分散剂基质以 0.1-10 重量份存在。在不同的实施方案中，噻二唑化合物相对于 100 重量份分散剂基质以大于 0.1-9，或者大于 0.1 至小于 5，或者 0.2 至小于 5 存在。噻二唑化合物与分散剂基质的相对量也可表示为 (0.1-10):100，或者 (>0.1-9):100(例如 (>0.5-9):100)，或者 (0.1 至小于 5):100，或者 (0.2 至小于 5):100。

[0073] 在一个实施方案中，分散剂基质相对于 1 重量份噻二唑化合物以 0.1-10 重量份存在。在不同的实施方案中，分散剂基质相对于 1 重量份噻二唑化合物以大于 0.1-9，或者大于 0.1 至小于 5，或者约 0.2 至小于 5 存在。分散剂基质与噻二唑化合物的相对量也可表示

为 (0.1-10):1,或者 (>0.1-9):1(例如 (>0.5-9):1),或者 (0.1 至小于 5):1,或者 (0.2 至小于 5):1。

[0074] 噻二唑官能化分散剂可衍生自包含以下分散剂的基质 :琥珀酰亚胺分散剂 (例如 N- 取代长链烯基琥珀酰亚胺,通常聚异丁烯琥珀酰亚胺)、曼尼希分散剂、含酯分散剂、脂肪烃基单羧酸酰化剂与胺或氨的缩合产物、烷基氨基苯酚分散剂、烃基胺分散剂、聚醚分散剂、聚醚胺分散剂、包含分散剂功能的粘度改进剂 (例如包含分散剂功能的聚合物粘度指数改进剂 (VM)) 或其混合物。在一个实施方案中,分散剂基质包含琥珀酰亚胺分散剂、含酯分散剂或曼尼希分散剂。

[0075] 在一个实施方案中,极压剂包括含硼化合物。含硼化合物包括硼酸酯 (在一些实施方案中,其也可称为硼酸化环氧化物)、硼酸化醇、硼酸化分散剂、硼酸化磷脂或其混合物。在一个实施方案中,含硼化合物可以为硼酸酯或硼酸化醇。

[0076] 硼酸酯可通过硼化合物和至少一种选自环氧化合物、卤代醇化合物、表卤醇化合物、醇及其混合物化合物反应而制备。醇包括二元醇、三元醇或较高级醇,对于一个实施方案,条件是羟基在相邻碳原子上,即邻近的。

[0077] 适于制备硼酸酯的硼化合物包括选自硼酸 (包括偏硼酸、原硼酸和四硼酸)、氧化硼、三氧化硼和硼酸烷基酯的各种形式。硼酸酯也可由硼卤化物制备。

[0078] 在一个实施方案中,合适的硼酸酯化合物包括硼酸三丙酯、硼酸三丁酯、硼酸三戊酯、硼酸三己酯、硼酸三庚酯、硼酸三辛酯、硼酸三壬酯和硼酸三癸酯。在一个实施方案中,硼酸酯化合物包括硼酸三丁酯、硼酸三 -2- 乙基己酯或其混合物。

[0079] 在一个实施方案中,含硼化合物为通常衍生自 N- 取代的长链烯基琥珀酰亚胺的硼酸化分散剂。在一个实施方案中,硼酸化分散剂包括聚异丁烯琥珀酰亚胺。硼酸化分散剂更详细地描述于美国专利 3,087,936 ;和专利 3,254,025 中。

[0080] 在一个实施方案中,硼酸化分散剂可与含硫化合物或硼酸酯组合使用。

[0081] 在一个实施方案中,极压剂为不同于硼酸化分散剂的。

[0082] 衍生出长链烯基的烃的数均分子量包括 350-5000,或者 500-3000,或者 550-1500 的范围。长链烯基可具有 550 或 750 或 950 至 1000 的数均分子量。

[0083] 将 N- 取代的长链烯基琥珀酰亚胺使用多种试剂,包括硼酸 (例如偏硼酸、原硼酸和四硼酸)、氧化硼、三氧化硼和硼酸烷基酯硼酸化。在一个实施方案中,硼酸化剂为硼酸,其可单独或与其它硼酸化剂组合使用。

[0084] 硼酸化分散剂可通过将硼酸化合物和 N- 取代的长链烯基琥珀酰亚胺混合并在合适温度如 80-250℃,或 90-230℃,或 100-210℃下加热它们直至发生所需反应而制备。硼化合物与 N- 取代的长链烯基琥珀酰亚胺的摩尔比可具有包括 10:1-1:4 或 4:1-1:3 在内的范围 ;或者硼化合物与 N- 取代的长链烯基琥珀酰亚胺的摩尔比可以为 1:2。作为选择,硼酸化分散剂中摩尔 B: 摩尔 N(即 B 原子 :N 原子) 之比可以为 0.25:1-10:1 或 0.33:1-4:1 或 0.2:1-1.5:1,或 0.25:1-1.3:1 或 0.8:1-1.2:1 或约 0.5:1。在进行反应中,可使用惰性液体。该液体可包括甲苯、二甲苯、氯苯、二甲基甲酰胺或其混合物。

[0085] 在一个实施方案中,润滑组合物进一步包含硼酸化磷脂。硼酸化磷脂可衍生自磷脂的硼酸化 (例如硼酸化可用硼酸进行)。磷脂和卵磷脂详细描述于 Encyclopedia of Chemical Technology,Kirk 和 Othmer,第 3 版,“Fats and Fatty Oils”,第 9 卷,第 795-831

页和“Lecithins”，第 14 卷，第 250-269 页中。

[0086]　磷脂可以为任何含有磷酸的类脂，例如卵磷脂或脑磷脂，或其衍生物。磷脂的实例包括磷脂酰胆碱、磷脂酰丝氨酸、磷脂酰肌醇、磷脂酰乙醇胺、磷脂酸及其混合物。磷脂可以为甘油磷脂、上列磷脂的甘油衍生物。通常，甘油磷脂在甘油残基上具有 1 或 2 个酰基、烷基或烯基。烷基或烯基可含有 8-30，或 8-25，或 12-24 个碳原子。合适的烷基或烯基的实例包括辛基、十二烷基、十六烷基、十八烷基、二十二烷基、辛烯基、十二碳烯基、十六碳烯基和十八碳烯基。

[0087]　磷脂可合成地制备或衍生自天然来源。合成磷脂可通过本领域技术人员已知的方法制备。天然衍生的磷脂通常通过本领域技术人员已知的程序提取。磷脂可衍生自动物或植物来源。有用的磷脂衍生自葵花籽。磷脂通常含有 35-60％磷脂酰胆碱、20-35％磷脂酰肌醇、1-25％磷脂酸和 10-25％磷脂酰乙醇胺，其中百分数为基于总磷脂的重量计。脂肪酸含量可以为 20-30 重量％棕榈酸、2-10 重量％硬脂酸、15-25 重量％油酸和 40-55 重量％亚油酸。

[0088]　摩擦改进剂可包括脂肪胺、酯如硼酸化甘油酯、脂肪亚磷酸酯、脂肪酰胺、脂肪环氧化物、硼酸化脂肪环氧化物、烷氧基化脂肪胺、硼酸化烷氧基化脂肪胺、脂肪酸的金属盐，或脂肪咪唑啉、羧酸和聚亚烷基 - 多胺的缩合产物。

[0089]　在一个实施方案中，润滑组合物可含有不同于如上所述描述为磷酸酯胺盐的极压剂的化合物的含磷或含硫抗磨剂。抗磨剂的实例可包括非离子磷化合物（通常具有具有 +3 或 +5 氧化态的磷原子的化合物）、金属二烷基二硫代磷酸盐（通常二烷基二硫代磷酸锌）、金属单 - 或二 - 烷基磷酸盐（通常磷酸锌）或其混合物。

[0090]　非离子磷化合物包括亚磷酸酯、磷酸酯或其混合物。

[0091]　在一个实施方案中，本发明润滑组合物进一步包含分散剂。分散剂可以为琥珀酰亚胺分散剂（如 N- 取代的长链烯基琥珀酰亚胺）、曼尼希分散剂、含酯分散剂、脂肪烃基单羧酸酰化剂与胺或氨的缩合产物、烷基氨基酚分散剂、烃基胺分散剂、聚醚分散剂或聚醚胺分散剂。

[0092]　在一个实施方案中，琥珀酰亚胺分散剂包括聚异丁烯 - 取代的琥珀酰亚胺，其中衍生出分散剂的聚异丁烯可具有 400-5000 或 950-1600 的数均分子量。

[0093]　琥珀酰亚胺分散剂和它们的制备方法更完整地描述于美国专利 4,234,435 和 3,172,892 中。

[0094]　合适的含酯分散剂通常为高分子量酯。这些材料更详细地描述于美国专利 3,381,022 中。

[0095]　在一个实施方案中，分散剂包括硼酸化分散剂。通常硼酸化分散剂包括琥珀酰亚胺分散剂，包括聚异丁烯琥珀酰亚胺，其中衍生出分散剂的聚异丁烯可具有 400-5000 的数均分子量。硼酸化分散剂更详细地描述于以上极压剂的描述内。

[0096]　分散剂粘度改进剂（通常称为 DVM）包括官能化聚烯烃，例如已用马来酸酐和胺的反应产物官能化的乙烯 - 丙烯共聚物、用胺官能化的聚甲基丙烯酸酯或与胺反应的酯化苯乙烯 - 马来酸酐共聚物也可用于本发明组合物中。

[0097]　腐蚀抑制剂包括 1- 氨基 -2- 丙醇、辛胺辛酸盐、十二碳烯基琥珀酸或酐和 / 或脂肪酸如油酸与多胺的缩合产物。

[0098] 金属减活剂包括苯并三唑（通常为甲苯基三唑）的衍生物、1,2,4- 三唑、苯并咪唑、2- 烷基二硫代苯并咪唑或 2- 烷基二硫代苯并噻唑。金属减活剂也可描述为腐蚀抑制剂。

[0099] 抑泡剂包括丙烯酸乙酯和丙烯酸 2- 乙基己酯和任选乙酸乙烯酯的共聚物。

[0100] 反乳化剂包括磷酸三烷基酯，和乙二醇、氧化乙烯、氧化丙烯或其混合物的各种聚合物和共聚物。

[0101] 倾点下降剂包括马来酸酐 - 苯乙烯的酯、聚甲基丙烯酸酯、聚丙烯酸酯或聚丙烯酰胺。

[0102] 密封溶胀剂包括 Exxon Necton-37™(FN 1380) 和 Exxon Mineral Seal Oil™(FN 3200)。

[0103] 本发明润滑油组合物可用于各种应用，例如轻型、中型和重型发动机油、工业发动机油、船用发动机油、曲轴用油、压缩机油、制冷机用油、烃压缩机油、非常低温润滑油和脂肪、高温润滑油和脂肪、钢缆润滑剂、纺织机油、制冷机油、航空航天润滑剂、航空用涡轮机油、变速器用油、汽轮机油、锭子油、自旋用油、牵引流体、变速器用油、塑料变速器用油、客车变速器用油、货车变速器用油、工业变速器用油、工业齿轮油、绝缘油、仪器用油、刹车流体、变速器流体、缓冲器油、热分布介质油、变压器用油、脂肪、链条用油、用于金属加工操作的最小量润滑剂、用于热和冷加工的油、用于水基金属加工液体的油、用于净油金属加工流体的油、用于半合成金属加工流体的油、用于合成金属加工流体的油、用于土壤勘探的钻井清净剂、液压油、可生物降解润滑剂或润滑油脂或蜡、链锯用油、脱模剂、模制流体、枪、手枪和步枪润滑剂或手表润滑剂和食品级许可润滑剂。

[0104] 机械装置优选选自轴承、齿轮、接头和导航。优选，机械装置在≥ 10℃至≤ 120℃的温度下操作。

实施例

[0105] 酯化合物的制备

[0106] 丙基庚醇由 BASF SE，Ludwigshafen 市购 [93.0 重量％ 2- 丙基 - 庚醇 ;2.9 重量％ 2- 丙基 -4- 甲基 - 己醇 ;3.9 重量％ 2- 丙基 -5- 甲基己醇和 0.2 重量％ 2- 异丙基庚醇]。

[0107] DIDA 例如作为 **Synative®** ES DIDA 由 BASF SE，Ludwigshafen 市购。己二酸二 -(2- 丙基庚基）酯 (DPHA) 的制备

[0108] 使可作为“丙基庚醇”由 BASF SE 得到的具有 10 个碳原子的醇的结构异构体 (2.4 摩尔）和己二酸 (1.0 摩尔）的混合物在高压釜中在惰性气体 (N_2) 下在 230℃的反应温度下在钛酸异丙基 - 丁酯 (0.001 摩尔）的存在下反应。在反应期间形成的水通过惰性气流 (N_2料流）从反应混合物中除去。在 180 分钟以后，将过量的醇在 50 毫巴的压力下通过蒸馏从混合物中除去。然后将因此所得的己二酸酯在 80℃下用 0.5％ NaOH 中和。其后，将有机相和水相分离，其后将有机相用水洗涤两次。在另一步骤中，通过在 180℃和 50 毫巴下将粗己二酸酯用蒸汽处理而提纯。然后通过使它在 150℃和 50 毫巴下经受 N_2料流而将酯干燥。最后，将酯与活性炭混合并使用流变剂 Supra-Theorit 在 80℃下在降低的压力下过滤。己二酸酯显示出根据 DIN51757，分别地 ASTM D 4052 测量在 20℃下 0.916g/cm^{3}的密度。

[0109] 润滑剂配制剂的制备

[0110] 表 1 :润滑剂配制剂 A 和 B(所有值为重量%)

[0111]

	具有 DIDA 的配制剂 A	具有 DPHA 的配制剂 B
PAO 6 (Nexbase® 2006，聚α烯烃，可由 Neste Oil N.V，比利时得到)	**52.0%**	**52.0%**
DIDA	**10.0%**	**-**
DPHA	**-**	**10.0%**
增稠剂(Lubrizol® 8406，聚异丁烯，可由 Lubrizol 得到)	**13.0%**	**13.0%**
增稠剂(来自 Lubrizol 的 Lubrizol® 8407)	**13.0%**	**13.0%**
Additives (Anglamol® 6004，可由 Lubrizol 得到的添加剂包)	**12.0%**	**12.0%**

[0112] 摩擦系数评估

[0113] 在 MTM(微牵引力测定仪)仪器中使用所谓的牵引力试验模式测试流体。以这种模式,摩擦系数以恒定的平均速度经一系列滑滚比 (SRR) 测量以得到牵引力曲线。SRR =滑动速度 / 平均夹带速度= 2(U1-U2)/(U1+U2),其中 U1 和 U2 分别为球和圆盘速度。

[0114] 用于实验的圆盘和球由钢 (AISI 52100) 构成,具有 750HV 的硬度和 <0.02μm 的 Ra。圆盘和球的直径分别为 45.0mm 和 19.0mm。牵引力曲线以 1,00GPa 接触压力、10-1000m/s 速度和不同的温度如 40℃和 100℃运行。滑滚比 (SRR) 为 50%并测量摩擦系数。各个试样 (20ml) 运行 3 次。

[0115] 评估结果

[0116] MTM 试验结果显示于图 1 和 2 中。每种情况下,上部曲线由配制剂 A 的评估得到,且下部曲线由配制剂 B 的评估得到。图 1 涉及试验在 40℃下进行时的结果,而图 2 涉及试验在 100℃下进行时的结果。

[0117] 每种情况下,包含根据本发明的酯的配制剂显示明显更低的摩擦系数。

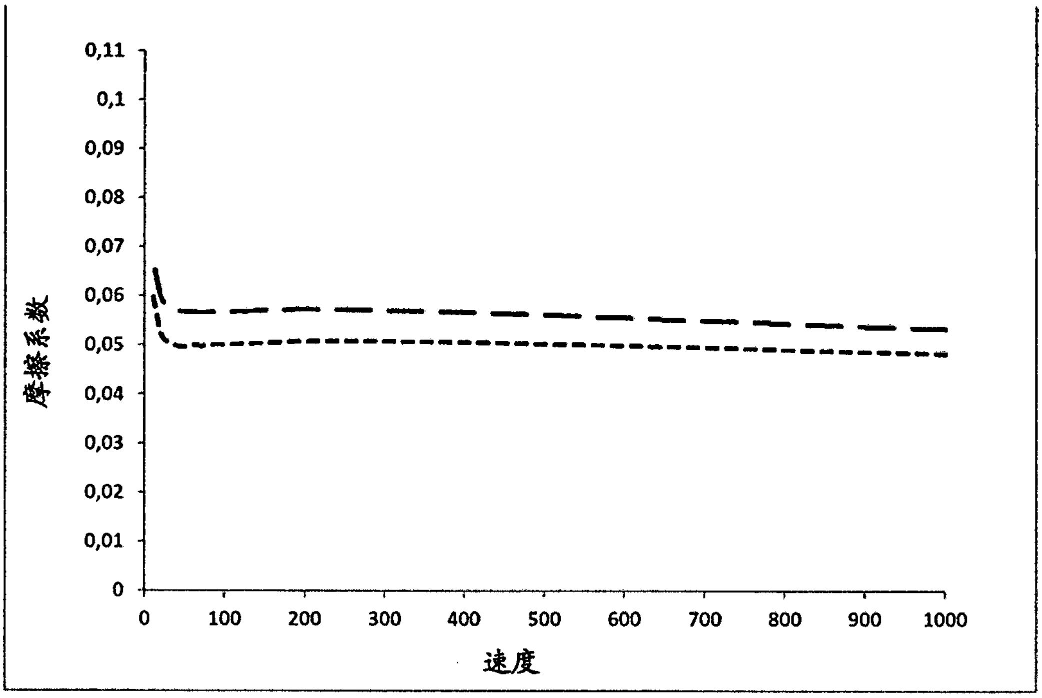

0,11
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
摩擦系数
0
100
200
300
400
500
600
700
800
900
1000
速度

图 1

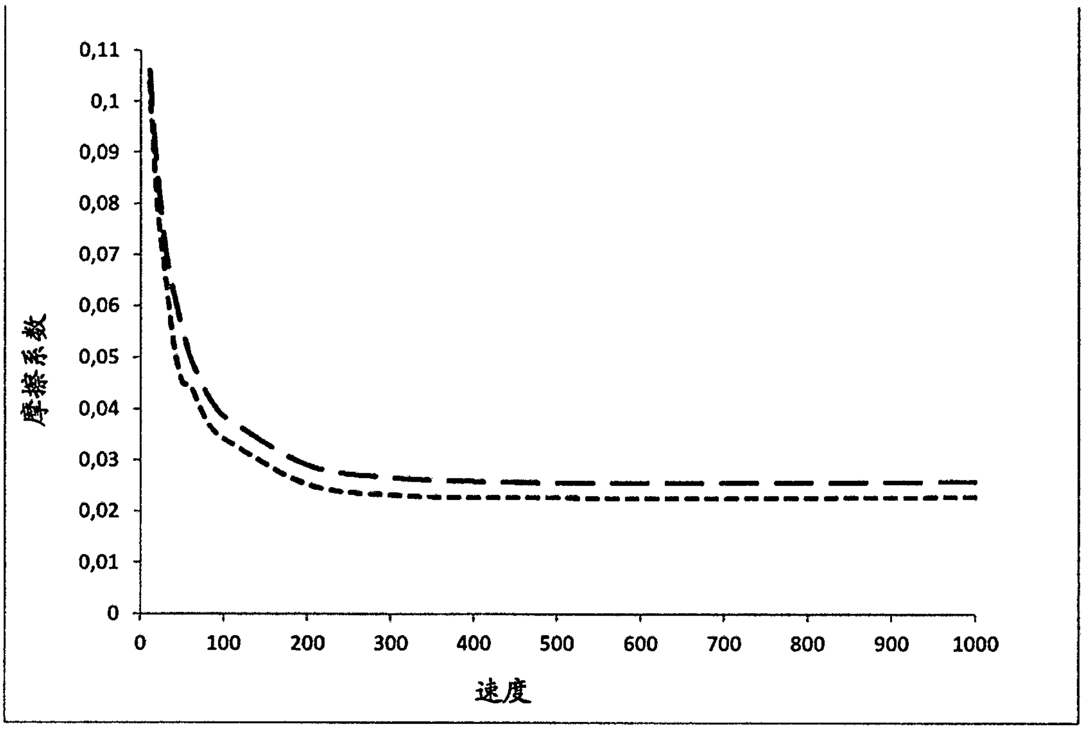

0,11
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
摩擦系数
0
100
200
300
400
500
600
700
800
900
1000
速度

图 2

Abstract

The presently claimed invention is directed to a method for reducing the friction coefficient of a lubricating oil composition in the lubrication of a mechanical device comprising formulating said lubricating oil composition with a carboxylic acid ester obtainable by reacting a mixture comprising at least on dicarboxylic acid and at least one branched C_{10} alcohol.