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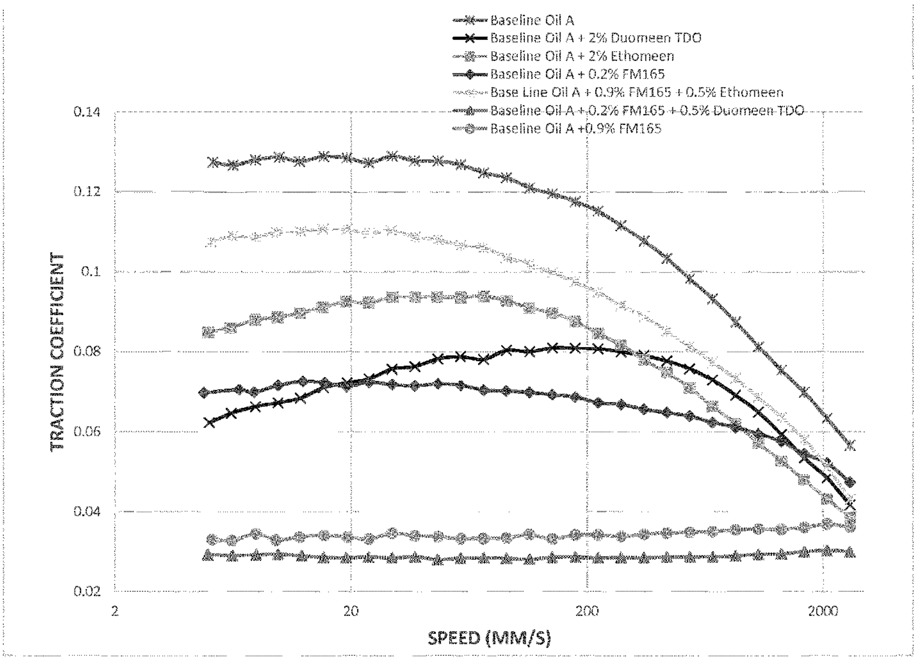
(54) **Title:** LUBRICATING COMPOSITION

Figure 1



(57) **Abstract:** A lubricating composition for use in the crankcase of an engine comprising (i) a base oil; (ii) one or more organo-molybdenum compounds at a level sufficient to provide from 50 to 500 ppmw of molybdenum; and (iii) from 0.2 wt% to 5 wt%, by weight of the lubricating composition, of one or more fatty diamine salt. The lubricating composition provides improvements in terms of reduced friction and wear, in addition to improved fuel economy performance.

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LUBRICATING COMPOSITION

Field of the Invention

The present invention relates to a lubricating oil composition, in particular to a lubricating oil composition which is suitable for lubricating internal combustion engines and which has improved friction and wear reduction and improved fuel economy.

Background of the Invention

Increasingly severe automobile regulations in respect of emissions and fuel efficiency are placing increasing demands on both engine manufacturers and lubricant formulators to provide effective solutions to improve fuel economy.

Optimising lubricants through the use of high performance base stocks and novel additives represents a flexible solution to a growing challenge.

Friction-reducing additives (which are also known as friction modifiers) are important lubricant components in reducing fuel consumption and various such additives are already known in the art.

Friction modifiers can be conveniently divided into two categories, that is to say, metal-containing friction modifiers and ashless (organic) friction modifiers.

Organo-molybdenum compounds are amongst the most common metal-containing friction modifiers. Typical organo-molybdenum compounds include molybdenum dithiocarbamates (MoDTC), molybdenum dithiophosphates (MoDTP), molybdenum amines, molybdenum alcoholates, and molybdenum alcohol-amides. WO9826030, WO9931113, WO9947629 and WO9966013 describe tri-nuclear molybdenum compounds for use in lubricating oil compositions.

However, the trend towards low-ash lubricating oil compositions has resulted in an increased drive to achieve low friction and improved fuel economy using ashless friction modifiers.

Ashless (organic) friction modifiers which have been used in the past typically comprise esters of fatty acids and polyhydric alcohols, fatty acid amides, amines derived from fatty acids and organic dithiocarbamate or dithiophosphate compounds. For example, US2016/0251590 discloses the use of fatty amine salts as friction modifiers for lubricants.

However, current strategies with regard to friction reduction for fuel economy oils are not sufficient to meet ever increasing fuel economy targets set by Original Equipment Manufacturers (OEMs). While there is a challenge to approach similar levels of friction modification using solely ashless friction modifiers, molybdenum friction modifiers typically outperform ashless friction modifiers in the boundary regime.

While organo-molybdenum compounds are useful for providing high levels of friction modification, there are also known limitations with these compounds. For example, molybdenum-based friction modifiers can negatively impact seals and the TEOST cleanliness test.

Given the increasing fuel economy demands placed on engines, there remains a need to further improve the friction reduction and fuel economy of internal combustion engines utilising lower levels of molybdenum-based friction modifiers.

Summary of the Invention

Accordingly, the present invention provides a lubricating composition for use in the crankcase of an engine comprising (i) a base oil; (ii) one or more organo-molybdenum compounds at a level sufficient to provide from 50 to 500 ppmw of molybdenum; and (iii) from 0.2 wt% to 5 wt%, by weight of the lubricating composition, of one or more fatty diamine salt.

Brief Description of the Drawings

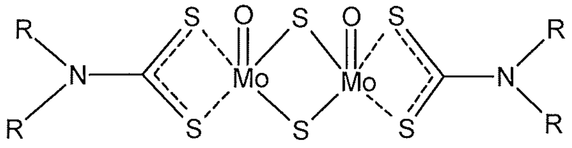
Figure 1 shows a plot of the results from the Examples.

Detailed Description of the Invention

There has now been surprisingly found by the present inventors that a lubricating oil composition comprising a combination of organo-molybdenum compound and fatty diamine salt friction reducing additives has improved friction and wear reduction and improved fuel economy, while requiring reduced levels of organo-molybdenum compounds.

An essential component of the lubricating compositions of the present invention is one or more organo-molybdenum compounds at a level sufficient to provide from 50 to 500 ppmw of molybdenum, preferably at a level sufficient to provide from 50 to 300 ppmw of molybdenum.

The organo-molybdenum compound for use herein is preferably selected from molybdenum dithiocarbamates (MoDTC), molybdenum dithiophosphates (MoDTP), molybdenum amines, molybdenum alcoholates, molybdenum alcohol-amides, and mixtures thereof. A preferred organo-molybdenum compound for use herein is a molybdenum dialkyldithiocarbamate (MoDTC) of formula (I):



(I)

wherein R is a C_2 to C_{10} straight chain or branched hydrocarbyl, preferably C_2 to C_{10} straight chain hydrocarbyl, even more preferably C_2 to C_6 straight chain hydrocarbyl, for example n-C_4.

Another essential component of the lubricating compositions of the present invention is one or more fatty diamine salt. Said fatty diamine salt is present from 0.2 wt% to 5 wt%, by weight of the lubricating composition, preferably, from 0.3 wt% to 3 wt% by weight of the lubricating composition, more preferably from 0.3 wt% to 2.0 wt% by weight of the lubricating composition.

As used in the present specification, the term "fatty diamine" relates to diamines of the formula II.

$$R^1{-}NH{-}R^2{-}NH_2 \quad \text{(II)},$$

wherein R^1 is selected from straight and branched, saturated and unsaturated C6-30 hydrocarbyl groups; and R^2 is $(CH_2)x$ where x is 2-6.

Preferably, R^1 is a straight or branched, saturated or unsaturated C8-22 hydrocarbyl. Examples of R^1 groups include, but are not limited to, coco alkyl, oleyl and tallow alkyl, rapeseed alkyl, soya alkyl, hexadecyl, tetradecyl, and mixtures thereof, and other fatty hydrocarbyl groups of vegetable or animal origin.

Examples of R^2 groups include, but are not limited to, ethylene, propylene, butylene, pentylene and hexylene. Preferably, R^2 is propylene, i.e. x is 3.

Preferably, the fatty diamine salt is a carboxylate salt, i.e. the carboxylic acid salt of a fatty diamine. The carboxylate salt of a fatty diamine is typically a dicarboxylate salt.

The carboxylic acids contemplated for use in the present invention includes, but are not limited to carboxylic acids of the formula R^3—COOH, where R^3 is a linear, branched or cyclic C1-6 hydrocarbyl group, preferably a linear or branched C1-5 alkyl group. Acetic acid and propionic acid, and their corresponding carboxylates, i.e. acetates and propionates, respectively, are particularly preferred.

The total amount of base oil incorporated in the lubricating oil composition of the present invention is preferably present in an amount in the range of from 60 to 92 wt%, more preferably in an amount in the range of from 75 to 90 wt% and most preferably in an amount in the range of from 75 to 88 wt%, with respect to the total weight of the lubricating oil composition.

There are no particular limitations regarding the base oil used in the present invention, and various conventional known mineral oils and synthetic oils may be conveniently used.

The base oil used in the present invention may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils.

Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

Naphthenic base oils have low viscosity index (VI) (generally 40-80) and a low pour point. Such base oils are produced from feed stocks rich in naphthenes and low in wax content and are used mainly for lubricants in which colour and colour stability are important, and VI and oxidation stability are of secondary importance.

Paraffinic base oils have higher VI (generally >95) and a high pour point. Said base oils are produced from feed stocks rich in paraffins, and are used for lubricants in which VI and oxidation stability are important.

Fischer-Tropsch derived base oils may be conveniently used as the base oil in the lubricating oil composition of the present invention, for example, the Fischer-Tropsch derived base oils disclosed in EP0776959, EP0668342, WO9721788, WO0015736, WO0014188, WO0014187, WO0014183, WO0014179, WO0008115, WO9941332, EP1029029, WO0118156 and WO0157166.

Synthetic processes enable molecules to be built from simpler substances or to have their structures modified to give the precise properties required.

Synthetic oils include hydrocarbon oils such as olefin oligomers (PAOs), dibasic acids esters, polyol esters, and dewaxed waxy raffinate. Synthetic hydrocarbon base oils sold by the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark) may be conveniently used.

Preferably, the base oil comprises mineral oils and/or synthetic oils which contain more than 80% wt of saturates, preferably more than 90 wt%, as measured according to ASTM D2007.

It is further preferred that the base oil contains less than 1.0 wt%, preferably less than 0.1 wt% of sulphur, calculated as elemental sulphur and measured according to ASTM D2622, ASTM D4294, ASTM D4927 or ASTM D3120.

Preferably, the viscosity index of the base oil is more than 80, more preferably more than 120, as measured according to ASTM D2270.

Preferably, the lubricating oil composition has a kinematic viscosity in the range of from 2 to 80 mm²/s at 100 °C, more preferably of from 3 to 70 mm²/s, most preferably of from 4 to 50 mm²/s.

The total amount of phosphorus in the lubricating oil composition of the present invention is preferably in the range of from 0.04 to 0.12 wt%, more preferably in the range of from 0.04 to 0.09 wt% and most preferably in the range of from 0.045 to 0.08 wt%, based on total weight of the lubricating oil composition.

The lubricating oil composition of the present invention preferably has a sulphated ash content of not greater than 2.0 wt%, more preferably not greater than 1.0 wt% and most preferably not greater than 0.8 wt%, based on the total weight of the lubricating oil composition.

The lubricating oil composition of the present invention preferably has a sulphur content of not greater than 1.2 wt%, more preferably not greater than 0.8 wt% and most preferably not greater than 0.2 wt%, based on the total weight of the lubricating oil composition.

The lubricating oil composition of the present invention may further comprise additional additives such as anti-oxidants, anti-wear additives, detergents, dispersants, additional friction modifiers, viscosity index improvers, pour point depressants, corrosion inhibitors, defoaming agents and seal fix or seal compatibility agents.

Antioxidants that may be conveniently used include those selected from the group of aminic antioxidants and/or phenolic antioxidants.

In a preferred embodiment, said antioxidants are present in an amount in the range of from 0.1 to 5.0 wt%, more preferably in an amount in the range of from 0.3 to

3.0 wt%, and most preferably in an amount in the range of from 0.5 to 1.5 wt%, based on the total weight of the lubricating oil composition.

Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl-α-naphthylamines, phenyl-β-naphthylamines and alkylated α-naphthylamines.

Preferred aminic antioxidants include dialkyldiphenylamines such as p,p'-dioctyl-diphenylamine, p,p'-di-α-methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butyldiphenylamine and mono-octyldiphenylamine, 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, 1-naphthylamine, arylnaphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine and 3,7-dioctylphenothiazine.

Preferred aminic antioxidants include those available under the following trade designations: "Sonoflex OD-3" (ex. Seiko Kagaku Co.), "Irganox L-57" (ex. Ciba Specialty Chemicals Co.) and phenothiazine (ex. Hodogaya Kagaku Co.).

Examples of phenolic antioxidants which may be conveniently used include C_7-C_9 branched alkyl esters of 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-

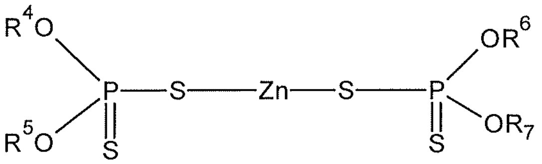
6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,6-d-t-butyl-α-dimethylamino-p-cresol, 2,2'-methylene-bis(4-alkyl-6-t-butylphenol) such as 2,2'-methylenebis(4-methyl-6-t-butylphenol, and 2,2-methylenebis(4-ethyl-6-t-butylphenol), bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethyleneglycol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycolbis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methyl-phenyl)propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 2,2'-thiobis(4,6-di-t-butylresorcinol), polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, 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 p-t-butylphenol - formaldehyde condensates and p-t-butylphenol - acetaldehyde condensates.

Preferred phenolic antioxidants include those available under the following trade designations: "Irganox L-135" (ex. Ciba Specialty Chemicals Co.), "Yoshinox SS" (ex. Yoshitomi Seiyaku Co.), "Antage W-400" (ex. Kawaguchi Kagaku Co.), "Antage W-500" (ex. Kawaguchi Kagaku Co.), "Antage W-300" (ex. Kawaguchi Kagaku Co.), "Irganox L109" (ex. Ciba Speciality Chemicals Co.), "Tominox 917" (ex. Yoshitomi Seiyaku Co.), "Irganox L115" (ex. Ciba Speciality Chemicals Co.), "Sumilizer GA80" (ex. Sumitomo Kagaku), "Antage RC" (ex. Kawaguchi Kagaku Co.), "Irganox L101" (ex. Ciba Speciality Chemicals Co.), "Yoshinox 930" (ex. Yoshitomi Seiyaku Co.).

The lubricating oil composition of the present invention may comprise mixtures of one or more phenolic antioxidants with one or more aminic antioxidants.

In a preferred embodiment, the lubricating oil composition may comprise a single zinc dithiophosphate or a combination of two or more zinc dithiophosphates as anti-wear additives, the or each zinc dithiophosphate being selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates.

Zinc dithiophosphate is a well known additive in the art and may be conveniently represented by general formula III;



(III)

wherein R^4 to R^7 may be the same or different and are each a primary alkyl group containing from 1 to 20 carbon atoms preferably from 3 to 12 carbon atoms, a secondary alkyl group containing from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms, an aryl group or an aryl group substituted with an alkyl group, said alkyl substituent containing from 1 to 20 carbon atoms preferably 3 to 18 carbon atoms.

Zinc dithiophosphate compounds in which R^4 to R^7 are all different from each other can be used alone or in admixture with zinc dithiophosphate compounds in which R^4 to R^7 are all the same.

Preferably, the or each zinc dithiophosphate used in the present invention is a zinc dialkyl dithiophosphate.

Examples of suitable zinc dithiophosphates which are commercially available include those available ex. Lubrizol Corporation under the trade designations "Lz 1097" and "Lz 1395", those available ex. Chevron Oronite under the trade designations "OLOA 267" and "OLOA 269R", and that available ex. Afton Chemical under the trade designation "HITEC 7197"; zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 677A", "Lz 1095" and "Lz 1371", that available ex. Chevron Oronite under the trade designation "OLOA 262" and that available ex. Afton Chemical under the trade designation "HITEC 7169"; and zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 1370" and "Lz 1373" and that available ex. Chevron Oronite under the trade designation "OLOA 260".

The lubricating oil composition according to the present invention may generally comprise in the range of from 0.4 to 1.2 wt% of zinc dithiophosphate, based on the total weight of the lubricating oil composition.

Additional or alternative anti-wear additives may be conveniently used in the composition of the present invention.

Typical detergents that may be used in the lubricating oil of the present invention include one or more salicylate and/or phenate and/or sulphonate detergents.

However, as metal organic and inorganic base salts which are used as detergents can contribute to the sulphated ash content of a lubricating oil composition, in a preferred embodiment of the present invention, the amounts of such additives are minimised.

In order to maintain a low sulphur level, salicylate detergents can be used.

Thus, in one embodiment, the lubricating oil composition of the present invention may comprise one or more salicylate detergents.

In order to maintain the total sulphated ash content of the lubricating oil composition of the present invention at a level of preferably not greater than 2.0 wt%, more preferably at a level of not greater than 1.0 wt% and most preferably at a level of not greater than 0.8 wt%, based on the total weight of the lubricating oil composition, said detergents are preferably used in amounts in the range of 0.05 to 20.0 wt%, more preferably from 1.0 to 10.0 wt% and most preferably in the range of from 2.0 to 5.0 wt%, based on the total weight of the lubricating oil composition.

Furthermore, it is preferred that said detergents, independently, have a TBN (total base number) value in the range of from 10 to 500 mg.KOH/g, more preferably in the range of from 30 to 350 mg.KOH/g and most preferably in the range of from 50 to 300 mg.KOH/g, as measured by

ISO 3771.

The lubricating oil compositions of the present invention may additionally contain an ash-free dispersant which is preferably admixed in an amount in the range of from 5 to 15 wt%, based on the total weight of the lubricating oil composition.

Examples of ash-free dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succininic acid esters disclosed in JP1367796, JP1667140, JP1302811 and JP1743435. Preferred dispersants include borated succinimides.

Examples of viscosity index improvers which may be conveniently used in the lubricating oil composition of the present invention include the styrene-butadiene copolymers, styrene-isoprene stellate copolymers and the polymethacrylate copolymer and ethylene-propylene copolymers. Such viscosity index improvers may be conveniently employed in an amount in the range of from 1 to 20 wt%, based on the total weight of the lubricating oil composition.

Polymethacrylates may be conveniently employed in the lubricating oil compositions of the present invention as effective pour point depressants.

Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating oil composition of the present invention as corrosion inhibitors.

Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating oil composition of the present invention as defoaming agents.

Compounds which may be conveniently used in the lubricating oil composition of the present invention as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

The lubricating compositions of the present invention may be conveniently prepared using conventional formulation techniques by admixing base oil with the organo-molybdenum compound and fatty diamine salt friction reducing additive together with and one or more other optional additives at a temperature of 60°C.

In another embodiment of the present invention, there is provided a method of lubricating an internal combustion engine comprising applying a lubricating oil composition as hereinbefore described thereto.

The present invention further provides the use of a lubricating composition as described herein for reducing friction.

The present invention further provides the use of a lubricating composition as described herein for reducing wear.

The present invention further provides the use of a lubricating composition as described herein for improving fuel economy.

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

Examples

A lubricating composition was formulated using conventional lubricant blending procedures ("Baseline Oil A") having the composition set out in Table 1 below.

The amounts of the components are given in wt%, based on the total weight of the compositions.

Table 1 (Composition of Baseline Oil A)

Component	Wt%
GTL 4[1]	74.91
GTL 3[1]	8.5
Additive package[2]	9.59
Viscoplex 3-201[3]	6.70
PPD[4]	0.03

1. Fischer-Tropsch derived base oils having a kinematic viscosity at 100°C (ASTM D445) of approximately 4 cSt and 3 cSt, respectively, which may be conveniently prepared by the process described in WO02070631.
2. Full SAPS additive package containing polyisobutylene succinimide dispersant, zinc alkyl dithiophosphate, overbased calcium alkyl salicylate detergent, borated dispersant and diphenylamine antioxidant.
3. Viscosity modifier commercially available from Evonik.
4. Poly alkyl methacrylate pour point depressant.

Baseline Oil A had a kV100 (as measured according to ASTM D445) of 8.02 mm^2/s, a kV40 (as measured according to ASTM D445) of 35.18 mm^2/s, a CCS at -35°C (as measured according to ASTM D5293) of 4330 mPa.s, and an HTHS (as measured according to ASTM D4741) of 2.74 mPa.s.

Various friction modifiers were added to Baseline Oil A in the amounts set out in Table 2 below to produce a number of Test Oils. The friction modifiers added to Baseline Oil A were FM165, a molybdenum dialkylthiocarbamate commercially available from Adeka; a fatty diamine friction reducing additive (Duomeen TDO commercially available from AkzoNobel); and other amine friction modifiers (e.g. Ethomeen, a fatty monoamine salt, commercially available from AkzoNobel).

Friction measurements were carried out on the compositions set out in Table 2 using a Mini-Traction Machine (MTM) manufactured by PCS Instruments.

The MTM Test was described by R.I. Taylor, E. Nagatomi, N.R. Horswill, D.M. James in "A screener test for the fuel economy potential of engine lubricants" presented at the 13th International Colloquium on Tribology, January 2002.

Friction coefficients were measured with the Mini-Traction Machine using the 'ball-on-disc' configuration.

The ball specimen was a polished steel ball bearing, 19.05 mm in diameter. The disc specimen was secured concentrically on a motor driven shaft. The disc specimen was secured concentrically on another motor driven shaft. The ball was loaded against the disc to create a point contact area with minimum spin and skew components. At the point of contact, a slide to roll ratio of 100% was maintained by adjusting the surface speed of the ball and disc.

The tests were run at a pressure of 1.25 GPa (load of 71N) at a temperature of 115°C at a variety of speeds from 2600 mm/s down to 5 mm/s as shown in Figure 1.

Each oil was tested using a new ball and a new disk for a total of 20 test scans, and the friction result was taken from the last three scans.

Friction coefficients of the relevant Test Oils (as set out in Table 2) were measured and the results are detailed in Table 2 below. In Table 2, the boundary friction coefficient is the averaged value at the low speeds from 0.05 m/s to 0.05 m/s, and the mixed friction coefficient is the averaged value at the higher speeds from 1.0 m/s to 2.6 m/s.

Table 2 - Results

	Test Oil:	Friction coefficient	
		Boundary	Mixed
1	Baseline Oil A	0.1207	0.0510
2	98 wt% Baseline Oil A + 2 wt% Duomeen TDO	0.0712	0.0535
3	98 wt% Baseline Oil A + 2 wt% Ethomeen	0.0907	0.0479
4	99.8 wt% Baseline Oil A + 0.2 wt% FM165 (=90ppmw Mo)	0.0714	0.0542
5	99.1 wt% Baseline Oil A + 0.9 wt% FM 165 (= 400ppmw)	0.0336	0.0361
6	98.6 wt% Baseline Oil A + 0.9wt% FM165 (=400ppmw Mo) + 0.5 wt% Ethomeen T12	0.1092	0.0569
7	99.3 wt% Baseline Oil A + 0.2 wt% FM165 (=90ppmw Mo) + 0.5 wt% Duomeen TDO	0.0288	0.0298

Figure 1 shows a plot of friction coefficient measurements in the boundary and mixed regimes as a function of speed for the compositions set out in Table 2.

Discussion

Lubrication regimes fall into four main categories: (1) Hydrodynamic, where the surfaces are completely separated by a fluid film, (2) Elastohydrodynamic, where the surfaces are separated by a very thin fluid film (3) Mixed, where the surfaces are partially separated with some asperity contact and (4) Boundary, where the surfaces are mostly in contact, even though a fluid film is present. The mixed and boundary regimes rely on chemical antiwear additives and/or friction modifiers, and the like, to reduce wear and friction.

Molybdenum containing friction modifiers are generally expected to perform well in reducing boundary friction and organic friction modifiers are thought to be more effective under mixed conditions.

As can be seen from Table 2, adding 2 wt% fatty diamine salt or monoamine salt alone to Baseline Oil A reduces the friction in the boundary regime slightly, but appears to increase mixed friction.

Adding 0.2 wt% (90ppmw)of the organo-molydenum compound alone to Baseline Oil A reduces both the boundary and mixed friction slightly.

Adding a much larger amount of the organo-molybdenum compound (0.9 wt%, 400ppmw) alone leads to reduced boundary and mixed friction, but using an undesirably large amount of molybdenum.

When 0.9 wt% (400 ppmw) of the organo-molybdenum compound is added to Baseline oil A with 0.5 wt% of a monoamine salt (Ethomeen), friction actually increased both in the boundary and mixed regime, near to the level of Baseline oil A.

However, when the organo-molybdenum compound at a lower level (90ppm, 0.2wt%) is combined with 0.5 wt% of a diamine salt, significant synergistic improvements in both boundary friction and mixed friction are seen.

CLAIMS

1. A lubricating composition for use in the crankcase of an engine comprising (i) a base oil; (ii) one or more organo-molybdenum compounds at a level sufficient to provide from 50 to 500 ppmw of molybdenum; and (iii) from 0.2 wt% to 5 wt%, by weight of the lubricating composition, of one or more fatty diamine salt.

2. A lubricating composition according to Claim 1 wherein the fatty diamine salt comprises a fatty diamine of formula II.

$$R^1\text{—NH—}R^2\text{—NH}_2 \quad \text{(II)},$$

wherein R^1 is selected from straight and branched, saturated and unsaturated C6-30 hydrocarbyl groups; and R^2 is $(CH_2)x$ where x is 2-6.

3. A lubricating composition according to Claim 1 or Claim 2 wherein the fatty diamine salt is a carboxylic acid salt of a fatty diamine.

4. A lubricating composition according to Claim 3 wherein the carboxylic acid is of the formula $R^3\text{—COOH}$, where R^3 is a linear, branched or cyclic C1-6 hydrocarbyl group, preferably a linear or branched C1-5 alkyl group.

5. A lubricating composition according to any of Claims 1 to 4 wherein the one or more organo-molybdenum compounds are selected from molybdenum dithiocarbamates, molybdenum dithiophosphates, molybdenum amines, molybdenum alcoholates, molybdenum alcohol-amides, and mixtures thereof.

6. A lubricating composition according to any of Claims 1 to 5 wherein the one or more organo-molybdenum compounds

comprises molybdenum dithiocarbamates.

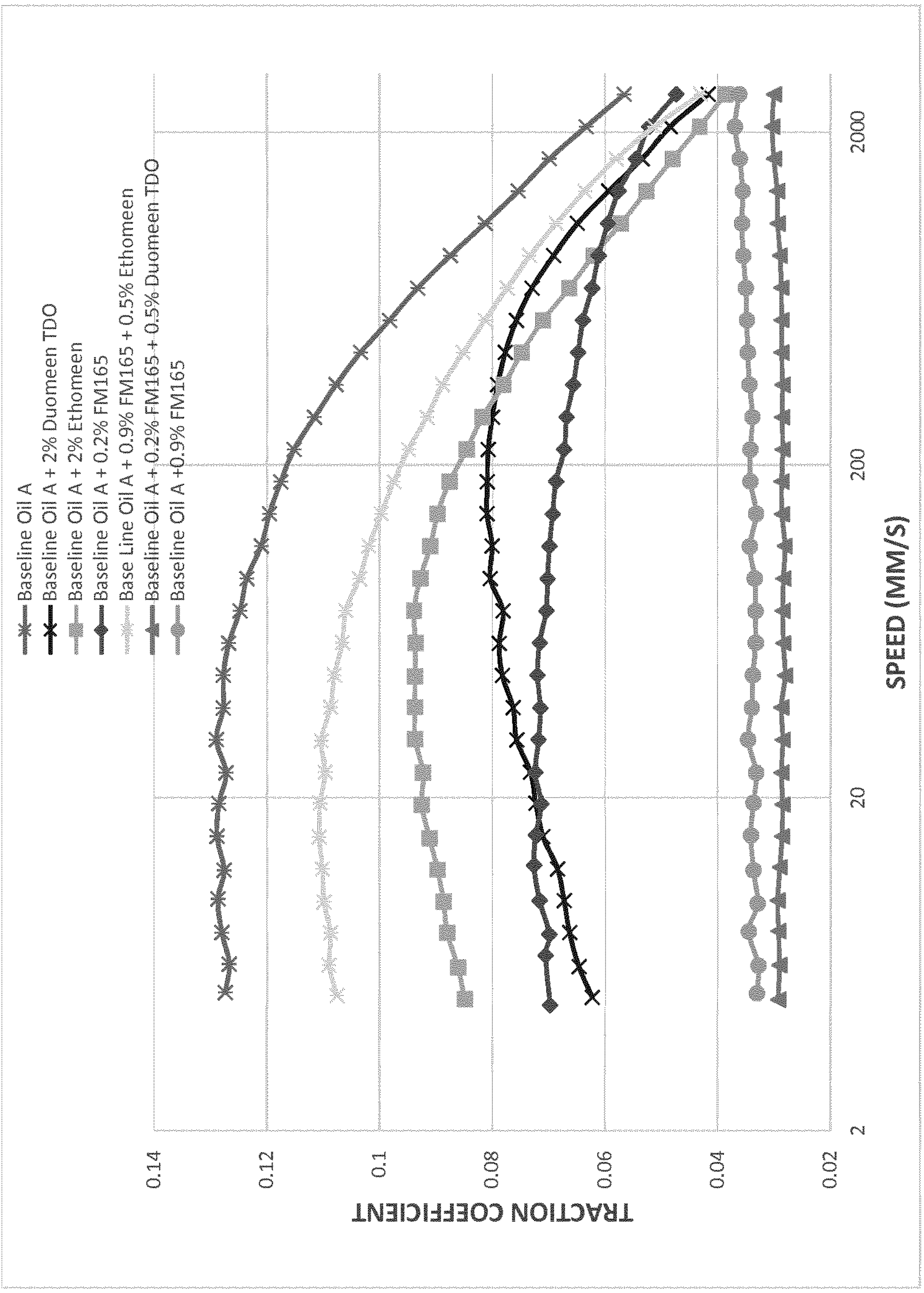
7. A lubricating composition according to any of Claims 1 to 6 wherein the base oil is a Fischer-Tropsch derived base oil.

8. Use of a lubricating composition according to any of Claims 1 to 9 in the crankcase of an engine, in order to reduce friction.

9. Use of a lubricating composition according to any one of claims 1 to 9 in the crankcase of an engine, in order to reduce wear.

10. Use of a lubricating composition according to any one of claims 1 to 9 in the crankcase of an engine, in order to improve fuel economy properties.

Figure 1


Baseline Oil A
Baseline Oil A + 2% Duomeen TDO
Baseline Oil A + 2% Ethomeen
Baseline Oil A + 0.2% FM165
Base Line Oil A + 0.9% FM165 + 0.5% Ethomeen
Baseline Oil A + 0.2% FM165 + 0.5% Duomeen TDO
Baseline Oil A +0.9% FM165
TRACTION COEFFICIENT
0.14
0.12
0.1
0.08
0.06
0.04
0.02
2
20
200
2000
SPEED (MM/S)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/067912

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M141/08
ADD.

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	WO 2017/149119 A1 (TOTAL MARKETING SERVICES [FR]) 8 September 2017 (2017-09-08) composition 2 of Tables 5 and 6 page 25, lines 1-10; example 2 page 2, line 16 - page 3, line 12 page 4, line 26 - page 5, line 21 page 8, lines 14-23 page 12, line 33 - page 13, line 16 -----	1-10
A	US 2017/275555 A1 (SOUTHBY MARK CLIFT [GB] ET AL) 28 September 2017 (2017-09-28) paragraphs [0001], [0013], [0014], [0022], [0065], [0075] paragraphs [0128] - [0137]; claims 1,12,13,15,19; tables 1-4 -----	1-10
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search
7 October 2019

Date of mailing of the international search report
18/10/2019

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International application No
PCT/EP2019/067912

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/046133 A1 (SHELL INT RES MIJ BV) 31 March 2016 (2016-03-31) page 1, lines 1-5 page 2, line 28 - page 4, line 14 page 13, lines 13-17; examples 1-6 -----	1-10
A	US 4 581 039 A (HORODYSKY ANDREW G [US]) 8 April 1986 (1986-04-08) column 1, lines 11-16, 53 - column 2, line 64 examples 1-4; tables 1,2 -----	1-10
A	WO 2010/146030 A1 (AKZO NOBEL CHEMICALS INT BV [NL]; KLINGBERG ANDERS [SE] ET AL.) 23 December 2010 (2010-12-23) page 5, line 29 - page 7, line 2; claims 1,2,10,12 -----	1-10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/067912

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017149119 A1	08-09-2017	BR 112018016701 A2	26-12-2018
		CN 108699474 A	23-10-2018
		EP 3423551 A1	09-01-2019
		FR 3048433 A1	08-09-2017
		JP 2019507230 A	14-03-2019
		KR 20180122337 A	12-11-2018
		WO 2017149119 A1	08-09-2017
US 2017275555 A1	28-09-2017	CN 106414686 A	15-02-2017
		EP 3158034 A1	26-04-2017
		JP 2017518426 A	06-07-2017
		US 2017275555 A1	28-09-2017
		WO 2015193395 A1	23-12-2015
WO 2016046133 A1	31-03-2016	BR 112017005843 A2	19-12-2017
		CN 107075403 A	18-08-2017
		EP 3197986 A1	02-08-2017
		JP 2017528588 A	28-09-2017
		RU 2017113940 A	24-10-2018
		WO 2016046133 A1	31-03-2016
US 4581039 A	08-04-1986	NONE	
WO 2010146030 A1	23-12-2010	BR PI1009699 A2	15-03-2016
		CA 2765759 A1	03-12-2010
		CN 102803453 A	28-11-2012
		EA 201270038 A1	30-10-2013
		EP 2443218 A1	25-04-2012
		ES 2430356 T3	20-11-2013
		SG 176261 A1	30-01-2012
		US 2012116107 A1	10-05-2012
		WO 2010146030 A1	23-12-2010
		ZA 201108994 B	29-08-2012