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C10M 2227/09 (2013.01); **C10N 2240/10**
(2013.01)(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 100 to 1000 ppmw of molybdenum; and (iii) from 0.2 wt % to 5.0 wt %, by weight of the lubricating composition, of one or more organic polymeric friction reducing additives, wherein the one or more organic polymeric friction reducing additives has a molecular weight ranging from 1000 to 30000 Daltons and is the reaction product of: a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls; b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; c) optionally at least one backbone moiety capable of linking together polymeric sub units; and d) optionally a chain terminating group. The lubricating composition provides improvements in terms of reduced friction and wear, in addition to improved fuel economy performance.

Figure 1

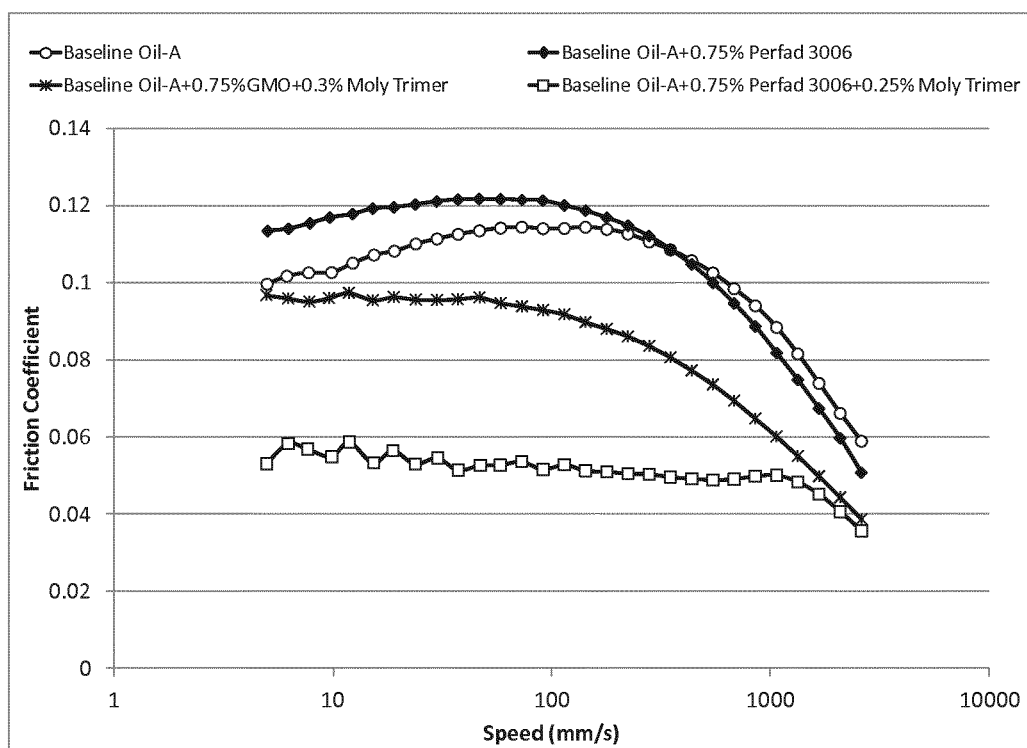
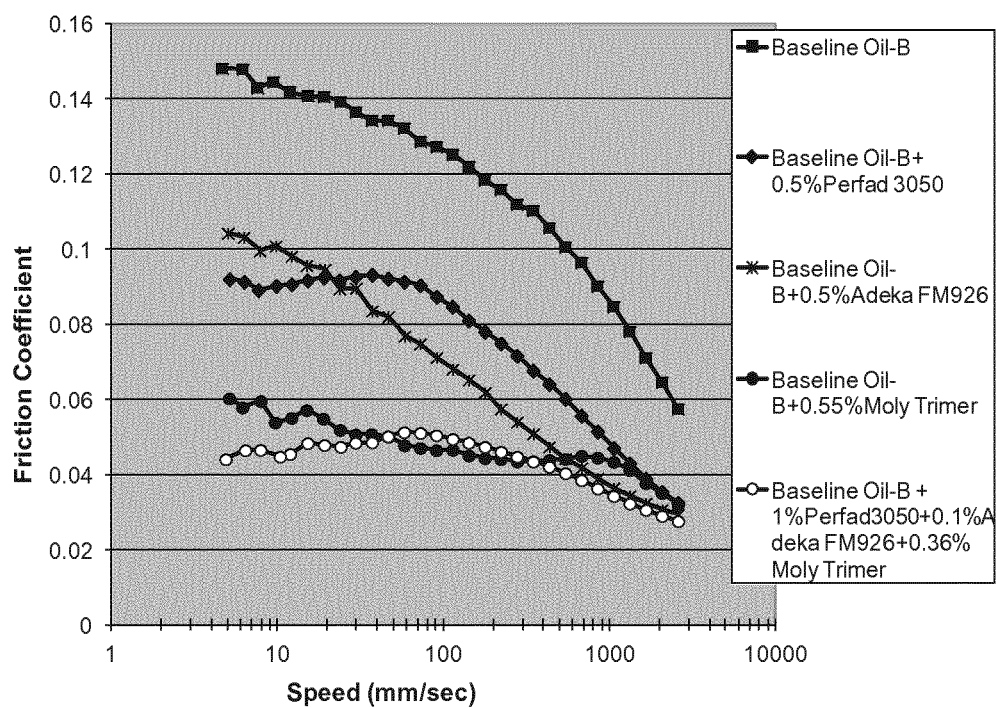


Figure 2



LUBRICATING COMPOSITION

[0001] 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.

[0002] 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.

[0003] Optimising lubricants through the use of high performance base stocks and novel additives represents a flexible solution to a growing challenge.

[0004] 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.

[0005] Friction modifiers can be conveniently divided into two categories, that is to say, metal-containing friction modifiers and ashless (organic) friction modifiers.

[0006] 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. WO-A-98/26030, WO-A-99/31113, WO-A-99/47629 and WO-A-99/66013 describe tri-nuclear molybdenum compounds for use in lubricating oil compositions.

[0007] 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.

[0008] 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.

[0009] 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.

[0010] 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.

[0011] 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.

[0012] WO2011/107739 discloses an automotive engine oil and/or fuel comprising a base stock and an organic polymeric friction reducing additive.

[0013] There has now been surprisingly found by the present inventors that a lubricating oil composition comprising a combination of organo-molybdenum compound and an organic polymeric friction reducing additive has

improved friction and wear reduction and improved fuel economy, while requiring reduced levels of organo-molybdenum compounds.

SUMMARY OF THE INVENTION

[0014] 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 100 to 1000 ppmw of molybdenum; and (iii) from 0.2 wt % to 5 wt %, by weight of the lubricating composition, of one or more organic polymeric friction reducing additives, wherein the one or more organic polymeric friction reducing additives has a molecular weight ranging from 1000 to 30000 Daltons and is the reaction product of:

[0015] a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;

[0016] b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;

[0017] c) optionally at least one backbone moiety capable of linking together polymeric sub units; and

[0018] d) optionally a chain terminating group.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 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.

[0020] FIG. 2 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 4.

DETAILED DESCRIPTION OF THE INVENTION

[0021] 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 100 to 1000 ppmw of molybdenum, preferably at a level sufficient to provide from 100 to 300 ppmw of molybdenum.

[0022] 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 molybdenum dithiocarbamate (MoDTC). In a preferred embodiment herein the organo-molybdenum compound contains tri-nuclear molybdenum (referred to herein as "moly trimer").

[0023] Another essential component of the lubricating compositions of the present invention is one or more organic polymeric friction reducing additives wherein the one or more organic polymeric friction reducing additives has a molecular weight ranging from 1000 to 30000 Daltons and is the reaction product of:

[0024] a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;

[0025] b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;

[0026] c) optionally at least one backbone moiety capable of linking together polymeric sub units; and

[0027] d) optionally a chain terminating group.

[0028] The hydrophobic polymeric sub unit preferably comprises a hydrophobic polymer which is a polyolefin or a polyalphaolefin, more preferably a polyolefin.

[0029] The polyolefin is preferably derived from a polymer of a monolefin having from 2 to 6 carbon atoms such as ethylene, propylene, butene and isobutene, more preferably isobutene, the said polymer containing a chain of from 15 to 500, preferably 50 to 200 carbon atoms.

[0030] The hydrophilic polymeric sub unit comprises a hydrophilic polymer selected from a polyether, a polyamide or a polyester. Examples of polyester include polyethylene terephthalate, polylactide and polycaprolactone. Examples of polyether include polyglycerol and polyalkylene glycol. In a particularly preferred embodiment the hydrophilic polymeric sub unit comprises a hydrophilic polymer which is a polymer of a water soluble alkylene glycol. A preferred hydrophilic polymeric sub unit comprises a hydrophilic polymer which is a polyethylene glycol (PEG), preferably PEG having a molecular weight of 300 to 5000 Daltons, more preferably 400 to 1000 Daltons, especially 400 to 800 Daltons. Alternatively, a mixed poly(ethylene-propylene glycol) or mixed poly(ethylene-butylene glycol) may be used provided they achieve the desired water solubility criteria. Exemplary hydrophilic polymer sub units for use in the present invention include PEG 400, PEG 600 and PEG 1000.

[0031] Other suitable hydrophilic polymeric sub units may comprise hydrophilic polymers which are polyethers and polyamides derived from diols and diamines containing acidic groups, e.g. carboxylic acid groups, sulphonyl groups (e.g. sulphonyl styrenic groups), amine groups (e.g. tetraethylene pentamine (TEPA) or polyethylene imine (PEI)), or hydroxyl groups (e.g. sugar based mono- or co-polymers).

[0032] The hydrophilic polymeric sub unit may be either linear or branched.

[0033] During the course of the reaction some of the hydrophobic and hydrophilic polymeric sub units may link together to form block copolymer units. Either or both of the hydrophobic and hydrophilic polymeric sub units may comprise functional groups which enable them to link with the other sub unit. For example, the hydrophobic polymeric sub unit may be derivatised so that it has a diacid/anhydride grouping by reaction with an unsaturated diacid or anhydride, for examples maleic anhydride. The diacid/anhydride can react by esterification with hydroxyl terminated hydrophilic polymeric sub units, for example a polyalkylene glycol. In a further example, the hydrophobic polymeric sub unit may be derivatised by an epoxidation reaction with a peracid, for example perbenzoic or peracetic acid. The epoxide can then react with hydroxyl and/or acid terminated hydrophilic polymeric sub units. In a further example, a hydrophilic polymeric sub unit which has a hydroxyl group may be derivatised by esterification with unsaturated mono carboxylic acids, for example vinyl acids, specifically acrylic or methacrylic acid. This derivatised hydrophilic polymeric sub unit can then react with a polyolefin hydrophobic polymeric sub unit by free radical copolymerisation.

[0034] A particularly preferred hydrophobic polymeric sub unit comprises polyisobutylene polymer which has been subjected to maleinisation to form polyisobutylene succinic anhydride (PIBSA) having a molecular weight in the range

of 300 to 5000 Daltons, preferably 500 to 1500 Daltons, especially 800 to 1200 Daltons. Polyisobutylene succinic anhydrides are commercially available compounds made by an addition reaction between poly(isobutene) having a terminal unsaturated group and maleic anhydride.

[0035] Such block copolymer units, if present, may be directly linked to each other and/or they may be linked together by the at least one backbone moiety. Preferably they are linked together by the at least one backbone moiety. The choice of backbone moiety capable of linking together the block copolymer units is governed by whether the linking of units is between two hydrophobic polymeric sub units, between two hydrophilic polymeric sub units or between a hydrophobic polymeric sub unit and a hydrophilic polymeric sub unit. Generally polyols and polycarboxylic acids form suitable backbone moieties. The polyol may be a diol, triol, tetrol, and/or related dimers or trimers or chain extended polymers of such compounds. Examples of suitable polyols include glycerol, neopentyl glycol, trimethyloethane, trimethylolpropane, trimethylolbutane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol. In a preferred embodiment, the polyol is a glycerol. Suitably the at least one backbone moiety is derived from a polycarboxylic acid, for example a di- or tricarboxylic acid. Dicarboxylic acids are preferred polycarboxylic acids, though branched chain dicarboxylic acids may also be suitable. Particularly suitable are straight chained dicarboxylic acids having a chain length of between 2 and 10 carbon atoms, for example oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic or sebacic acid. Unsaturated dicarboxylic acids such as maleic acid may also be suitable. A particularly preferred polycarboxylic acid backbone moiety to link units is adipic acid. Alternative linking backbone moieties are low molecular weight alkenyl succinic anhydrides (ASA) such as C₁₈ASA.

[0036] In any of the organic polymeric friction reducing additives different or same backbone moieties can be used to link together such block copolymer units. When present the number of block copolymer units in the organic polymeric friction reducing additive typically ranges from 1 to 20 units, preferably from 1 to 15, more preferably from 1 to 10 and especially 1 to 7 units.

[0037] When the product of the reaction ends in a reactive group (e.g. as with the OH in PEG), it may be desirable or useful in some circumstances to introduce a chain terminating group to the end of the product of the reaction. It is, for example, particularly simple to attach a carboxylic acid to an exposed hydroxyl group on PEG via an ester linkage. In this respect, any fatty carboxylic acid would be suitable. Suitable fatty acids include C₁₂-C₂₂ linear saturated, branched saturated, linear unsaturated and branched unsaturated acids, including, but not limited to lauric acid, erucic acid, isostearic acid, palmitic acid, oleic acid, and linoleic acid, preferably palmitic acid, oleic acid and linoleic acid. A particularly preferred fatty acid for combination with the surfactant is tall oil fatty acid (TOFA), a derivative of tall oil, which is primarily oleic acid.

[0038] The organic polymeric friction reducing additive used herein has a molecular weight of from 1000 to 30000 Daltons, preferably from 1500 to 25000, more preferably from 2000 to 20000 Daltons. Generally a composition comprising the organic polymeric friction reducing additive will comprise a range of polymer chains of different lengths such that there will be a range of molecular masses in a

particular composition. In such a case it is desirable that a substantial portion of the organic polymeric friction reducing additive molecules are within the above mentioned size ranges.

[0039] The organic polymeric friction reducing additive herein has a desired acid value of less than 20, preferably less than 15.

[0040] In one embodiment of the invention the organic polymeric friction reducing additive is the reaction product of:

[0041] a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;

[0042] b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; and

[0043] d) a chain terminating group.

[0044] For such an embodiment the preferred molecular weight range is 1000 to 3000 Daltons and the desired acid value is less than 15.

[0045] In a separate embodiment of the invention the organic polymeric friction reducing additive is the reaction product of:

[0046] a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;

[0047] b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; and

[0048] c) at least one backbone moiety capable of linking together polymeric sub units.

[0049] For such an embodiment, the preferred molecular weight range is 3000 to 25000, more preferably 5000 to 20000 Daltons. The desired acid value is preferably less than 10, more preferably less than 7.

[0050] In another embodiment, the organic polymeric friction reducing additive is the reaction product of:

[0051] a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;

[0052] b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;

[0053] c) at least one backbone moiety capable of linking together polymeric sub units; and

[0054] d) a chain terminating group.

[0055] For such an embodiment the preferred molecular weight range is 2000 to 10000, more preferably 2000 to 5000 Daltons. The desired acid value is preferably less than 15, more preferably less than 10.

[0056] The ingredients of the reactions a), b) and c) when present and d) when present may be mixed in a single step process or they may be mixed together in a multi step-process.

[0057] The organic polymeric friction reducing additive described hereinabove is commercially available from Croda under the trade names Perfad 3050 and Perfad 3006.

[0058] The organic polymeric friction reducing additive is present at a level of from 0.2 wt % to 5.0 wt %, preferably at a level of from 0.3 wt % to 3.0 wt %, more preferably 0.2 wt % to 1.5 wt %, by weight of the lubricating composition.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] 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.

[0063] 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.

[0064] 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.

[0065] 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 EP-A-776959, EP-A-668342, WO-A-97/21788, WO-00/15736, WO-00/14188, WO-00/14187, WO-00/14183, WO-00/14179, WO-00/08115, WO-99/41332, EP-1029029, WO-01/18156 and WO-01/57166.

[0066] Synthetic processes enable molecules to be built from simpler substances or to have their structures modified to give the precise properties required.

[0067] 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.

[0068] 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.

[0069] 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.

[0070] Preferably, the viscosity index of the base oil is more than 80, more preferably more than 120, as measured according to ASTM D2270.

[0071] 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.

[0072] 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.

[0073] 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.

[0074] 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.

[0075] 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.

[0076] A particularly preferred additional additive for use herein in combination with the organo-molybdenum compound and the organic polymeric friction reducing additive described hereinabove is a hydroxy alkyl amine friction modifier, such as that commercially available from Adeka under the trade name Adeka FM926. When present, the hydroxy alkyl amine friction modifier is present at a level of from 0.2 wt % to 3.0 wt %, more preferably at a level of from 0.3 wt % to 1.0 wt %, by weight of the lubricating composition.

[0077] Antioxidants that may be conveniently used include those selected from the group of aminic antioxidants and/or phenolic antioxidants.

[0078] 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.

[0079] Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl- α -naphthylamines, phenyl- β -naphthylamines and alkylated α -naphthylamines.

[0080] Preferred aminic antioxidants include dialkyldiphenylamines such as p,p'-diocetyl-diphenylamine, p,p'-di- α -methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butyl-diphenylamine and mono-octyl-diphenylamine, bis (dialkylphenyl)amines such as di-(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octylphenyl-1-naphthylamine and n-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine and 3,7-dioctylphenothiazine.

[0081] 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.).

[0082] Examples of phenolic antioxidants which may be conveniently used include C₇-C₉ branched alkyl esters of 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic

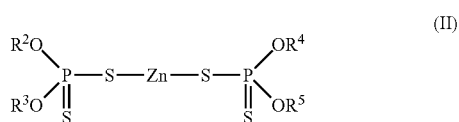
acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 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-di-t-butyl-4-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], triethyleneglycol-bis[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-methylphenyl)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.

[0083] 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 Specialty Chemicals Co.), "Tominox 917" (ex. Yoshitomi Seiyaku Co.), "Irganox L115" (ex. Ciba Specialty Chemicals Co.), "Sumilizer GA80" (ex. Sumitomo Kagaku), "Antage RC" (ex. Kawaguchi Kagaku Co.), "Irganox L101" (ex. Ciba Specialty Chemicals Co.), "Yoshinox 930" (ex. Yoshitomi Seiyaku Co.).

[0084] The lubricating oil composition of the present invention may comprise mixtures of one or more phenolic antioxidants with one or more aminic antioxidants.

[0085] 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.

[0086] Zinc dithiophosphate is a well known additive in the art and may be conveniently represented by general formula II;



wherein R^2 to R^5 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.

[0087] Zinc dithiophosphate compounds in which R^2 to R^5 are all different from each other can be used alone or in admixture with zinc dithiophosphate compounds in which R^2 to R^5 are all the same.

[0088] Preferably, the or each zinc dithiophosphate used in the present invention is a zinc dialkyl dithiophosphate.

[0089] 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".

[0090] 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 total weight of the lubricating oil composition.

[0091] Additional or alternative anti-wear additives may be conveniently used in the composition of the present invention.

[0092] 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.

[0093] 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.

[0094] In order to maintain a low sulphur level, salicylate detergents can be used.

[0095] Thus, in one embodiment, the lubricating oil composition of the present invention may comprise one or more salicylate detergents.

[0096] 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.

[0097] 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.

[0098] 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.

[0099] Examples of ash-free dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succinic acid esters disclosed in Japanese Patent Nos. 1367796, 1667140, 1302811 and 1743435. Preferred dispersants include borated succinimides.

[0100] 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.

[0101] Polymethacrylates may be conveniently employed in the lubricating oil compositions of the present invention as effective pour point depressants.

[0102] 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.

[0103] Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating oil composition of the present invention as defoaming agents.

[0104] 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.

[0105] The lubricating compositions of the present invention may be conveniently prepared using conventional formulation techniques by admixing base oil with the organomolybdenum compound and polymeric friction reducing additive together with and one or more other optional additives at a temperature of 60° C.

[0106] 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.

[0107] The present invention further provides the use of a lubricating composition as described herein for reducing friction.

[0108] The present invention further provides the use of a lubricating composition as described herein for reducing wear.

[0109] The present invention further provides the use of a lubricating composition as described herein for improving fuel economy.

[0110] 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

[0111] A lubricating composition was formulated using conventional lubricant blending procedures (“Baseline Oil A”) having the composition set out in Table 1 below.

[0112] 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	79.50
Additive package ²	13.30
Viscoplex 3-201 ³	6.90
PPD ⁴	0.30

¹A Fischer-Tropsch derived base oil having a kinematic viscosity at 100° C. (ASTM D445) of approximately 4 cSt which may be conveniently prepared by the process described in WO 02/070631.

²Full SAPS additive package containing polyisobutylene succinimide dispersant, zinc alkyl dithiophosphate, overbased calcium alkyl salicylate detergent, borated dispersant and diphenylamine antioxidant.

³Viscosity modifier commercially available from Evonik.

⁴Poly alkyl methacrylate pour point depressant.

[0113] Baseline Oil A had a kV100 (as measured according to ASTM D445) of 8.02 mm²/s, a kV40 (as measured according to ASTM D445) of 35.18 mm²/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.

[0114] 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 an organo-molybdenum compound (molybdenum dithiocarbamate (MoDTC) containing trinuclear molybdenum, referred to in Table 2 and FIG. 1 as “Moly Trimer”), a polymeric friction reducing additive (Perfad 3006 commercially available from Croda) and glycerol monooleate, a well known and generally available friction modifier.

[0115] Friction measurements were carried out on the compositions set out in Table 2 using a Mini-Traction Machine (MTM) manufactured by PCS Instruments.

[0116] 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.

[0117] Friction coefficients were measured with the Mini-Traction Machine using the ‘ball-on-disc’ configuration.

[0118] 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.

[0119] 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 FIGS. 1 and 2.

[0120] 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.

[0121] 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
Baseline Oil A	0.107	0.074
99.25 wt % Baseline Oil	0.118	0.067
A + 0.75 wt % Perfad 3006		
96.25 wt % Baseline Oil A +	0.112	0.035
3% Moly Trimer +		
0.75% glycerol		
monooleate		
99 wt % Baseline Oil A +	0.055	0.044
0.25% Moly Trimer +		
0.75% Perfad 3006		

[0122] FIG. 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.

[0123] A further lubricating composition was formulated using conventional lubricant blending procedures (“Baseline Oil B”) having the composition set out in Table 3 below.

TABLE 3

(Composition of Baseline Oil B)	
Component:	Wt %
GTL4 ¹	80.70
SV277 ²	7.20
Additive Package ³	12.1

¹A Fischer-Tropsch derived base oil having a kinematic viscosity at 100° C. (ASTM D445) of approximately 4 cSt which may be conveniently prepared by the process described in WO 02/070631.

²Hydrogenated styrene-diene copolymer.

³Additive package containing polyisobutylene succinimide dispersant, zinc alkyl dithiophosphate, overbased calcium alkyl phenate and sulphonate detergents, and phenolic antioxidant.

[0124] Baseline Oil B had a kV100 (as measured according to ASTM D445) of 8.93 mm²/s, a kV40 (as measured according to ASTM D445) of 45.20 mm²/s, a VI of 183, an HTHS at 150° C. (as measured according to ASTM D4741) of 2.52 cPs, an HTHS at 100° C. (as measured according to ASTM D4741) of 5.55 cPs.

[0125] Various friction modifiers were added to Baseline Oil B in the amounts set out in Table 4 below to produce a number of Test Oils. The friction modifiers added to Baseline Oil B were an organo-molybdenum compound (molybdenum dithiocarbamate (referred to in Table 4 and FIG. 2 as ‘holy Trimer’)), a polymeric friction reducing additive (Perfad 3050 commercially available from Croda) and Adeka FM926 (a hydroxyalkylamine friction modifier commercially available from Adeka).

[0126] Friction coefficients of the relevant Test Oils (as set out in Table 4) were measured using the MTM test method described above and the results are detailed in Table 4 below.

In Table 4, 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 4

Results		
Test Oil:	Friction coefficient	
	Boundary	Mixed
Baseline Oil B	0.141	0.076
99.5 wt % Baseline Oil B + 0.5 wt % Perfad 3050	0.092	0.039
99.5 wt % Baseline Oil B + 0.5 wt % Adeka FM926	0.094	0.034
99.45 wt % Baseline Oil B + 0.55 wt % Moly Trimer	0.048	0.040
wt % Baseline Oil A + 1% Perfad 3050 + 0.1 wt % Adeka FM926 + 0.36 wt % Moly Trimer	0.048	0.033

[0127] FIG. 2 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 4.

Discussion

[0128] 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.

[0129] 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.

[0130] As can be seen from Table 2, adding 0.75% polymeric organic friction modifier alone to Baseline Oil A reduces the friction in the mixed regime, but appears to increase boundary friction.

[0131] When 170 ppm Mo (3 wt % MoDTC) is added to Baseline Oil A with 0.75% of a common organic friction modifier, GMO, we see a slight reduction in boundary friction and significant reduction in mixed friction.

[0132] When only 140 ppm Mo (0.25 wt % MoDTC) is added with 0.75% polymeric organic friction modifier, surprisingly, we see a dramatic reduction in boundary friction and a further reduction in mixed friction. This appears to be a truly synergistic effect and could not have been predicted from the other results in Table 2.

[0133] The polymeric organic friction modifier appears to increase boundary friction alone, yet enables very low boundary friction in combination with the molybdenum containing friction modifier, which is very much lower than the molybdenum containing friction modifier in combination with a conventional organic friction modifier, GMO.

[0134] Adding 0.5% of an alternative polymeric organic friction modifier (Perfad 3050) to Baseline Oil B significantly reduces boundary and mixed friction.

[0135] It appears the hydroxy alkyl amine friction modifier (Adeka FM926) is more effective in the mixed regime, but a little less effective at reducing boundary friction.

[0136] When 300 ppm Mo (0.55 wt % molybdenum dithiocarbonate containing trinuclear molybdenum (identified in Tables 2 and 4, and in FIGS. 1 and 2, as 'Moly trimer')) is added to Baseline Oil B we see a very large drop in both boundary and mixed friction, though mixed friction appears to be marginally higher than that delivered by the organic friction modifiers.

[0137] When a combination of 200 ppm Mo (0.36 wt % Moly trimer) is added to Baseline Oil B, in combination with 1% of Perfad 3050 and 0.1% the hydroxy alkyl amine (Adeka FM925) friction modifier we see very low friction in both boundary and mixed regime. Surprisingly, the boundary friction is lower using only 200 ppm Mo in this combination, when compared with that measured with 300 ppm Mo alone.

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 100 to 1000 ppmw of molybdenum; and (iii) from 0.2 wt % to 5.0 wt %, by weight of the lubricating composition, of one or more organic polymeric friction reducing additives, wherein the one or more organic polymeric friction reducing additives has a molecular weight ranging from 1000 to 30000 Daltons and is the reaction product of:

- a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
- a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;
- optionally at least one backbone moiety capable of linking together polymeric sub units; and
- optionally a chain terminating group.

2. A lubricating composition according to claim 1 wherein the one or more organic polymeric friction reducing additives is the reaction product of:

- a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
- a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;
- at least one backbone moiety capable of linking together polymeric sub units; and
- a chain terminating group.

3. A lubricating composition according to claim 1 wherein the one or more organic polymeric friction reducing additives is the reaction product of:

- a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
- a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; and
- at least one backbone moiety capable of linking together polymeric sub units.

4. A lubricating composition according to claim 1 wherein the one or more organic polymeric friction reducing additives is the reaction product of:

- a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
 - b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; and
 - d) a chain terminating group.
5. A lubricating composition according to claim 1 wherein the hydrophobic polymeric sub unit comprises a hydrophobic polymer which is a polyolefin.
6. A lubricating composition according to claim 1 wherein the hydrophobic polymeric sub unit comprises polyisobutylene polymer which has been subjected to maleinisation to form polyisobutylene succinic anhydride having a molecular weight in the range of 300 to 5000 Daltons.
7. A lubricating composition according to claim 1 wherein the hydrophilic polymeric sub unit comprises a hydrophilic polymer which is a polyethylene glycol.
8. A lubricating composition according to claim 1 wherein the backbone moiety is chosen from a polyol, a polycarboxylic acid and mixtures thereof.
9. A lubricating composition according to claim 1 wherein the chain terminating group is any fatty carboxylic acid.
10. A lubricating composition according to claim 1 wherein the reaction product comprises some block copolymer units formed from linking together during the reaction of some of the hydrophobic and hydrophilic polymeric sub units.
11. A lubricating composition according to claim 10 wherein the number of block copolymer units range from 1 to 20.
12. A lubricating composition according to claim 1 wherein the one or more organo-molybdenum compounds is selected from molybdenum dithiocarbamates (MoDTC), molybdenum dithiophosphates (MoDTP), molybdenum amines, molybdenum alcoholates, and molybdenum alcohol-amides, and mixtures thereof.
13. A lubricating composition according to claim 12 wherein the one or more organo-molybdenum compounds is a molybdenum dithiocarbamate (MoDTC).
14. A lubricating composition according to claim 1 additionally comprising a hydroxy alkyl amine
15. A lubricating composition according to claim 1 wherein the base oil is a Fischer-Tropsch derived base oil.
16. (canceled)
17. (canceled)
18. (canceled)
19. A method of lubricating an internal combustion engine comprising:
- applying a lubricating composition to a surface in a crankcase of the engine, wherein the lubricating composition comprises (i) a base oil; (ii) one or more

- organo-molybdenum compounds at a level sufficient to provide from 100 to 1000 ppmw of molybdenum; and
 - (iii) from 0.2 wt % to 5.0 wt %, by weight of the lubricating composition, of one or more organic polymeric friction reducing additives, wherein the one or more organic polymeric friction reducing additives has a molecular weight ranging from 1000 to 30000 Daltons and is the reaction product of:
- a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
 - b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;
 - c) optionally at least one backbone moiety capable of linking together polymeric sub units; and
 - d) optionally a chain terminating group.
20. A method according to claim 19 wherein the one or more organic polymeric friction reducing additives is the reaction product of:
- a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
 - b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides;
 - c) at least one backbone moiety capable of linking together polymeric sub units; and
 - d) a chain terminating group.
21. A method according to claim 19 wherein the one or more organic polymeric friction reducing additives is the reaction product of:
- a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
 - b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; and
 - c) at least one backbone moiety capable of linking together polymeric sub units.
22. A method according to claim 19 wherein the one or more organic polymeric friction reducing additives is the reaction product of:
- a) a hydrophobic polymeric sub unit which comprises a hydrophobic polymer selected from polyolefins, polyacrylics and polystyrenyls;
 - b) a hydrophilic polymeric sub unit which comprises a hydrophilic polymer selected from polyethers, polyesters, polyamides; and
 - a chain terminating group.

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