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(54) **Method for lubricating surfaces**

(57) A method of lubricating an aluminum alloy surface or a ferrous surface which comprises supplying to said surface a lubricating oil composition comprising an oil of lubricating viscosity and an effective friction reduc-

ing amount of an oil soluble trinuclear organo-molybdenum compound.

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Description

[0001] This invention relates to methods of lubricating surfaces, in particular, to methods of lubricating surfaces in internal combustion engines.

[0002] Developments in automotive vehicle and engine designs has led to use of a more varied range of materials for manufacture of the engine components. In particular aluminum alloys are increasingly being used to manufacture engine components.

[0003] In accordance with a first aspect of the present invention there is provided a method of lubricating an aluminum alloy surface, which comprises supplying to said surface a lubricating oil composition comprising an oil of lubricating viscosity, preferably in a major amount, and an oil-soluble trinuclear organo-molybdenum compound.

[0004] It has been found that the trinuclear organo-molybdenum additive will substantially reduce friction and surface wear on the aluminum containing alloy surfaces to an extent not observed with dinuclear-organo-molybdenum compounds.

[0005] The aluminum alloy suitably comprises an aluminum-silicon alloy, which may additionally contain a proportion of copper and/or magnesium. Suitably the aluminum alloy has a hardness of 100-150 Hv, preferably 110-130 Hv and more preferably of about 120 Hv. Suitably, the aluminum alloy has a density of 2.0-3.0 gcm⁻³, preferably, 2.4-2.8 gcm⁻³, and more preferably, about 2.6 gcm⁻³.

[0006] Typically the trinuclear organo-molybdenum additive is used so as to provide 25 to 1000 ppm (parts per million, by weight), preferably 200 to 750 ppm, more preferably 400 to 600 ppm, and advantageously 500 ppm of elemental molybdenum in the lubricating oil compositions (as determined by ASTM D5185).

[0007] The lubricating oil composition of the first aspect of the invention may further comprise an oil soluble, zinc dihydrocarbyl dithiophosphate (ZDDP) produced from a primary alcohol, herein after referred to as primary ZDDP. Suitably, primary ZDDP comprises at least 50%, preferably at least 75%, more preferably at least 90%, and advantageously comprises substantially 100% ZDDP produced from primary.

[0008] The lubricating oil composition suitably comprises 0.2 to 1.0 mass %, preferably 0.4 to 0.8 mass %, and more preferably 0.6 to 0.75 mass % primary ZDDP.

[0009] The method according the first aspect of the invention suitably involves provision of lubrication between an aluminum alloy surface and a non-aluminum alloy surface, such as a ferrous surface, for example.

[0010] A second aspect of this invention is an internal combustion engine having one or more component parts made from an aluminum alloy, and contained in a reservoir in the engine, a lubricating oil composition for lubricating said parts comprising an oil of lubricating viscosity, preferably in a major amount, and an oil-soluble, trinuclear organo-molybdenum compound. The reservoir in the engine may be a crankcase sump in four-stroke engines, from where it is distributed around the engine for lubrication. The invention is applicable to two-stroke and four-stroke spark-ignited and compression-ignited engines.

[0011] A third aspect of the invention relates to the use of a lubricating oil composition comprising an oil of lubricating viscosity and an oil-soluble, trinuclear organo-molybdenum compound to lubricate an aluminum alloy surface.

[0012] A fourth aspect of the invention provides the use of an oil-soluble, trinuclear organo-molybdenum compound in a lubricating oil composition to reduce the friction between surfaces, one of which comprising an aluminum alloy.

[0013] In accordance with a fifth aspect of the present invention there has been discovered a method of providing lubrication between two ferrous surfaces, one of the ferrous surfaces comprising a chromium containing iron alloy conforming to British Standard BS EN31 and the other ferrous surfaces comprises a cast iron alloy conforming to British Standard BS EN1452, which method comprises supplying to said surface a lubricating oil composition comprising an oil of lubricating viscosity, preferably in a major amount, and an oil-soluble trinuclear organo-molybdenum compound.

[0014] It has been found that the trinuclear organo-molybdenum additive will substantially reduce friction and surface wear on the ferrous surfaces to an extent not observed with dinuclear-organo-molybdenum compounds.

[0015] Typically the trinuclear organo-molybdenum additive is used so as to provide 25 to 1000 ppm (parts per million, by weight), preferably 200 to 750 ppm, more preferably 400 to 600 ppm, and advantageously 500 ppm of elemental molybdenum in the lubricating oil compositions (as determined by ASTM D5185).

[0016] The lubricating oil composition of the fifth aspect of the invention may further comprise an oil soluble, zinc dihydrocarbyl dithiophosphate (ZDDP) made from secondary alcohol, hereinafter referred to as secondary ZDDP. Suitably, the secondary ZDDP comprises at least 55%, preferably at least 79% and more preferably at least 85%, and may comprise substantially 100% ZDDP made from secondary alcohol.

[0017] The lubricating oil composition suitably comprises 0.2 to 1.0 mass %, preferably 0.4 to 0.8 mass %, and more preferably 0.6 to 0.75 mass % secondary ZDDP.

[0018] A sixth aspect of this invention is an internal combustion engine having a component part made from a chromium containing ferrous alloy conforming with British Standard BS EN31 adjacent a component part made from an iron alloy conforming with British Standard BS EN1452, both component parts being contained in a reservoir in the engine, a lubricating oil composition for lubricating said parts comprising an oil of lubricating viscosity, preferably in a major amount,

and an oil-soluble, trinuclear organo-molybdenum compound. The reservoir in the engine maybe a crankcase sump in four-stroke engines, from where it is distributed around the engine for lubrication, The invention is applicable to two-stroke and four-stroke spark-ignited and compression-ignited engines.

[0019] A seventh aspect of the invention relates to the use of a lubricating oil composition comprising an oil of lubricating viscosity an oil-soluble, trinuclear organo-molybdenum compound to provide lubrication between a chromium containing ferrous alloy surface conforming with British Standard BS EN31 and an iron alloy surface conforming with British Standard BS EN1452.

[0020] An eighth aspect of the invention provides the use of an oil-soluble, trinuclear organo-molybdenum compound in a lubricating oil composition to reduce the friction between a chromium containing ferrous alloy surface conforming with British Standard BS EN31 and an iron alloy surface conforming with British Standard BS EN1452.

[0021] The methods of any aspect of this invention are especially applicable to the lubrication of spark-ignited or compression-ignited two-stroke or four-stroke internal combustion engines which have parts or components made from the specified materials. Examples of such components include the cam shaft, especially the cam lobes; pistons, especially the piston skirt; cylinder liners; and valves.

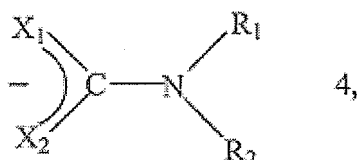
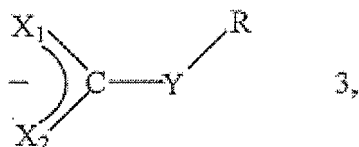
[0022] As examples of suitable oil-soluble, trinuclear organo-molybdenum compounds, there may be mentioned dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates and sulfides of molybdenum and mixtures thereof.

[0023] Additionally, the molybdenum compounds may be acidic molybdenum compounds. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., molybdenum trioxide or similar acidic molybdenum compounds.

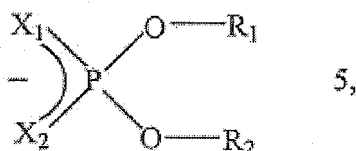
[0024] A group of trinuclear organo-molybdenum compounds useful in the lubricating compositions of this invention are those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof wherein L represents independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. In the instance n is 3, 2 or 1, appropriately charged ionic species is required to confer electrical neutrality to the trinuclear molybdenum compound. The ionic species may be of any valence, for example, monovalent or divalent. Further the ionic species may be negatively charged, *i.e.* an anionic species, or may be positively charged, *i.e.* a cationic species or a combination of an anion and a cation. Such terms are known to a skilled person in the art The ionic species may be present in the compound through covalent bonding, *i.e.* coordinated to one or more molybdenum atoms in the core, or through electrostatic bonding or interaction as in the case of a counter-ion or through a form of bonding intermediate between covalent and electrostatic bonding. Examples of anionic species include disulfide, hydroxide, an alkoxide, an amide and a thiocyanate or derivate thereof; preferably the anionic species is disulfide ion. Examples of cationic species include an ammonium ion and a metal ion, such as an alkali metal, alkaline earth metal or transition metal, ion, preferably an ammonium ion, such as $[\text{NR}_4]^+$ where R is independently H or alkyl group, more preferably R is H, *i.e.* $[\text{NH}_4]^+$. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0025] The ligands are independently selected from the group of:





and



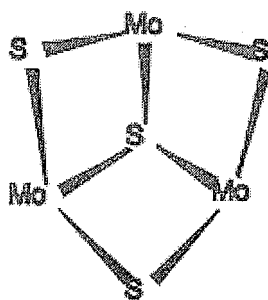
mid mixtures thereof, wherein X, X₁, X₂, and Y are independently selected from the group of oxygen and sulfur, and wherein R₁, R₂, and R are independently selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. More preferably, each ligand has the same hydrocarbyl group.

[0026] The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following:

1. Hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group).
2. Substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxy, mercapto, alkylmercapto, nitro, nitroso and sulfoxy).
3. Hetero substituents, that is substituents which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

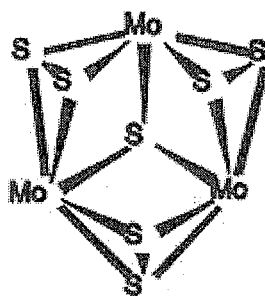
[0027] Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. For example, the number of carbon atoms in each group will generally range between 1 to 100, preferably from 1 to 30, and more preferably between 4 to 20. Preferred ligands include dialkyldithiophosphate, alkylxanthate, and dialkyldithiocarbamate, and of these dialkyldithiocarbamate is more preferred. Organic ligands containing two or more of the above functionalities are also capable of serving as ligands and binding to one or more of the cores. Those skilled in the art will realize that formation of the compounds of the present invention requires selection of ligands having the appropriate charge to balance the core's charge.

[0028] Compounds having the formula Mo₃S_kL_nQ_z have cationic cores surrounded by anionic ligands and are represented by structures such as



6

and



7,

and have net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. Four monoanionic ligands are preferred. Without wishing to be bound by any theory, it is believed that two or more trinuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate. Such structures fall within the scope of this invention. This includes the case of a multidentate ligand having multiple connections to a single core. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

[0029] Oil-soluble or oil-dispersible trinuclear molybdenum compounds can be prepared by reacting in the appropriate liquid(s) and/or solvent(s) a molybdenum source such as $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n(\text{H}_2\text{O})$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetralkylthiuram disulfide. Other oil-soluble or oil-dispersible trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n(\text{H}_2\text{O})$, a ligand source such as tetralkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur-abstracting agent such cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[\text{M}^1]_2[\text{Mo}_3\text{S}_7\text{A}_6]$, where M^1 is a counter ion, and A is a halogen such as Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s) and/or solvent(s) to form an oil-soluble or oil-dispersible trinuclear molybdenum compound. The appropriate liquid and/or solvent may be, for example, aqueous or organic.

[0030] A compound's oil solubility or dispersibility may be influenced by the number of carbon atoms in the ligand's organo groups. In the compounds employed in the present invention, at least 21 total carbon atoms should be present among all the ligand's organo groups. Preferably, the ligand source chosen has a sufficient number of carbon atoms in its organo groups to render the compound soluble or dispersible in the lubricating composition.

[0031] The molybdenum compound is preferably a trinuclear molybdenum dithiocarbamate.

[0032] Natural oils useful as the oil of lubricating viscosity (also known as basestocks) in this invention include animal oils and vegetable oils (*e.g.* castor, lard oil) liquid petroleum oils and hydrotreated, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0033] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification or etherification constitute a class of known synthetic lubricating oils useful as basestocks in this invention. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (*e.g.* methyl-poly isopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); 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.

[0034] Another suitable class of synthetic lubricating oils useful in this invention comprises the esters of dicarboxylic acids (e.g. 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, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (i-butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dicicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0035] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0036] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetrachthyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tertbutylphenyl) silicate, hexa-(4-methyl-2-pentoxo) disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g. tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0037] Unrefined, refined and refined oils can be used in the lubricating oil compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improved one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed, or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0038] Lubricating oil compositions for use in any aspect of the present invention may also contain any of the conventional additives listed below (including any additional friction modifiers) which are typically used in a minor amount, e.g. such an amount so as to provide their normal attendant functions. Typical amounts for individual components are also set forth below. All the values listed are stated as mass percent active ingredient in the total lubricating oil composition.

ADDITIVE	MASS % (Broad)	MASS% (preferred)
Ashless Dispersant	0.1 - 20	1 - 8
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitors	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 6	0.1 - 4
Anti-oxidant	0 - 5	0.01 - 3
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Anti-foaming Agent	0 - 5	0.001 - 0.15
Supplemental Anti-wear Agents	0 - 5	0 - 2
Additional Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0 - 6	0.01 - 4

[0039] The individual additives may be incorporated into a basestock in any convenient way. Thus, each of the components can be added directly to the basestock by dispersing or dissolving it in the basestock at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

[0040] Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate (or additive package) that is subsequently blended into basestock to make a finished lubricating oil composition. Use of such concentrates is conventional. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final lubricating oil composition when the concentrate is combined with a predetermined amount of base oil.

[0041] The concentrate is conveniently made in accordance with the method described in U.S. 4,938,880. That patent

describes making a pre-mix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 200°C. Thereafter, the pre-mix is cooled to at least 85°C and the additional components are added.

[0042] The final crankcase lubricating oil composition may employ from 2 to 20 mass % and preferably 4 to 15 mass % of the concentrate (or additive package), the remainder being base oil.

[0043] Ashless dispersants maintain in suspension oil-insoluble matter resulting from oxidation of the oil during wear or combustion. They are particularly advantageous for preventing precipitation of sludge and formation of varnish, particularly in gasoline engines.

[0044] Ashless dispersants comprise an oil-soluble polymeric hydrocarbon backbone bearing one or more functional groups that are capable of associating with particles to be dispersed. Typically, the polymer backbone is by amine, alcohol, amide, or ester polar moieties, often via a bridging group. The ashless dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0045] The oil-soluble polymeric hydrocarbon backbone of these dispersants is typically derived from an olefin polymer or polyene, especially polymers comprising a major molar amount (*i.e.* greater than 50 mole %) of a C₂ to C₁₈ olefin (*e.g.* ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ olefin. The oil-soluble polymeric hydrocarbon backbone may be a homopolymer (*e.g.* polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (*e.g.* copolymers of ethylene and an alpha-olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, for example, 1 to 10 mole %, is an α,ω -diene, such as a C₃ to C₂₂ non-conjugated diolefin (for example, a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). Preferred are polyisobutenyl (Mn 400-2500, preferably 950-2200) succinimide dispersants.

[0046] The viscosity modifier (VM) functions to impart high and low temperature operability to a lubricating oil composition. The VM used may have that sole function, or may be multifunctional.

[0047] Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic ester, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

[0048] Metal-containing or ash-forming detergents may be present and these function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and expending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acid organic compound. The salts may contain a substantially stoichiometric amount of the metal in which they are usually described as normal or neutral salts, and would typically have a total base number (TBN), as may be measured by ASTM D-2896 of from 0 to 80. It is possible to include large amounts of a metal base by leading an excess of a metal compound such as an oxide or hydroxide with an acid gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (*e.g.* carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically from 250 to 450 or more. Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali, *e.g.* sodium, potassium, lithium and magnesium. Preferred are neutral or overbased calcium and magnesium phenates and sulfonates, especially calcium.

[0049] Other friction modifiers include oil-soluble amines, amides, imidazolines, amine oxides, amidoamines, nitriles, alkanolamides, alkoxyated amines and ether amines; polyol esters; and esters of polycarboxylic acids.

[0050] Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P₂S₅ and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound may be used but oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

[0051] ZDDP provides excellent wear protection at a comparatively low cost and also functions as an antioxidant. However, there is some evidence that phosphorus in lubricant can shorten the effective life of automotive emission catalysts. Accordingly, the lubricating oil compositions of the invention preferably contain no more than 0.8 wt %, such as from 50 ppm to 0.06 wt %, of phosphorus. Independently of the amount of phosphorus, the lubricating oil composition

preferably has no more than 0.5 wt %, preferably from 50 ppm to 0.3 wt %, of sulfur, the amounts of sulfur and of phosphorus being measured in accordance with ASTM D5185.

[0052] Oxidation inhibitors or antioxidants reduce the tendency of basestocks to deteriorate in service, which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, ashless oil-soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil-soluble copper compound as described in U.S. 4,867,890, and molybdenum-containing compounds.

[0053] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0054] Copper- and lead-bearing corrosion inhibitors may be used, but are typically not required in the lubricating oil compositions of the present invention. Typically such compounds are thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4-thiadiazoles, such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932, are typical. Other similar material are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are thio and polythio sulfenamides of thiadiazoles such as those described in GB-A-1,560,830. Benzotriazoles derivatives also fall within this class of additive. When these compounds are included in the lubricating oil composition, they are preferably present in an amount not exceeding 0.2 wt. % active ingredient.

[0055] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP-A-330 522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

[0056] Pour point depressants, otherwise known as lube oil improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well-known. Typical of those additives, which improve the low temperature fluidity of the fluid, are C₈ and C₁₈ dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

[0057] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0058] In this specification, the term "comprising" (or cognates such as "comprises") means the presence of stated features, integers, steps or components, but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. If the term "comprising" (or cognates) is used herein, the term "consisting essentially of" (and its cognates) is within its scope and is a preferred embodiment; consequently the term "consisting of" (and its cognates) is within the scope of "consisting essentially of" and is a preferred embodiment thereof.

[0059] The terms "oil-soluble" or "oil-dispersible" do not mean that the compounds are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. They do mean, however, that the compounds are, for instance, soluble or stably dispersible in the oil to an extent sufficient to exert their intended effect in the environment in which the composition is employed. Moreover, the additional incorporation of other additives such as those described above may affect the solubility or dispersibility of the compounds.

[0060] The term "major amount" means in excess of 50 mass % of the composition.

[0061] The term "minor amount" means less than 50 mass % of the composition.

[0062] The invention is further illustrated by the following examples which are not to be considered as limitative of its scope. All percentages are by weight active ingredient content of an additive without regard for carrier or diluent oil.

EXAMPLES

[0063] All of the following experiments were carried out using were obtained using a Cameron Plint reciprocating pin on plate tribometer, using the following test protocol:

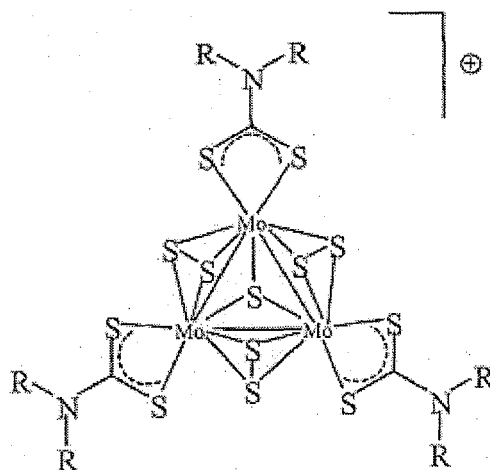
Test duration	8 hours
Load (N)	185
Stroke length (mm)	10
Frequency (Hz)	1
Temperature (°C)	100

[0064] The surface materials used are as set out below:

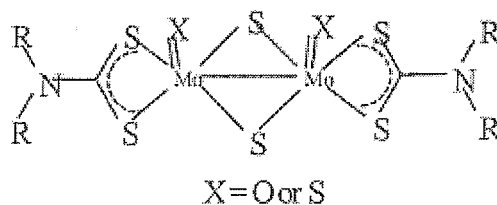
							Hardness	Density
BS EN31	C	O	Si	Cr	Mn	Fe	(Hv)	(g/cm ³)
Wt%	0.64	-	0.55	1.57	0.49	96.75	185	7.75
Al-Si Alloy	C	O	Si	Cu	Al	Mg		
Wt%	4.44	2.29	22.62	1.12	68.25	1.27	120	2.62
BS 1452	C	O	Si	Mo	Mn	Fe		
Wt%	9.32	1.91	2.74	0.44	0.71	84.88	150	7.01

[0065] The coefficients of friction and wear coefficients for the lubrication of various surface combinations with a each of the following lubricant compositions, were measured:

1. a Group III base oil having a kinematic viscosity at 100°C of 4.2 $\mu\text{m}^2\text{s}^{-1}$ (CSt);
2. a composition containing the base oil of composition 1 and 500 ppm of molybdenum as trinuclear molybdenum dithiocarbamate, having a structural formula as shown below,



3. a composition containing the base oil of composition 1 and 500 ppm of molybdenum as dinuclear molybdenum dithiocarbamate, having a structural formula as shown below,



4. a composition according to composition 2 additionally comprising a minor amount of a secondary ZODP additive, and
5. a composition according to composition 2 additionally comprising a minor amount of a primary ZDDP.

Example 1 BS EN1452 pin on Al-Si alloy plate

[0066] A comparison of friction coefficient for Compositions 1, 2 and 3 is set out in Table 1 and Graph 1. A comparison of wear coefficient for Compositions 1, 2 and 3 is set out in Graph 2.

[0067] It can be seen from Table 1 and Graph 1 below, that Composition 2, containing the trinuclear organo-molybdenum compound, exhibits a significantly lower friction coefficient than Composition 1 or 2. Furthermore, the coefficient of friction for Composition 2 continues to reduce as the test proceeds, unlike Composition 1 or 3, for which the friction coefficient increases as the test proceeds.

[0068] A comparison of the percentage improvement in friction coefficient of Composition 2 compared to Composition 1 at equivalent points in the test also illustrates the generally increasing reduction of friction coefficient of Composition 2 compared to Composition 1. In addition, Table 1 illustrates that Composition 2 performs significantly more effectively at reducing the coefficient of friction than Composition 3, which generally performs less well than Composition 1 (as indicated by the negative prefix).

Graph 1

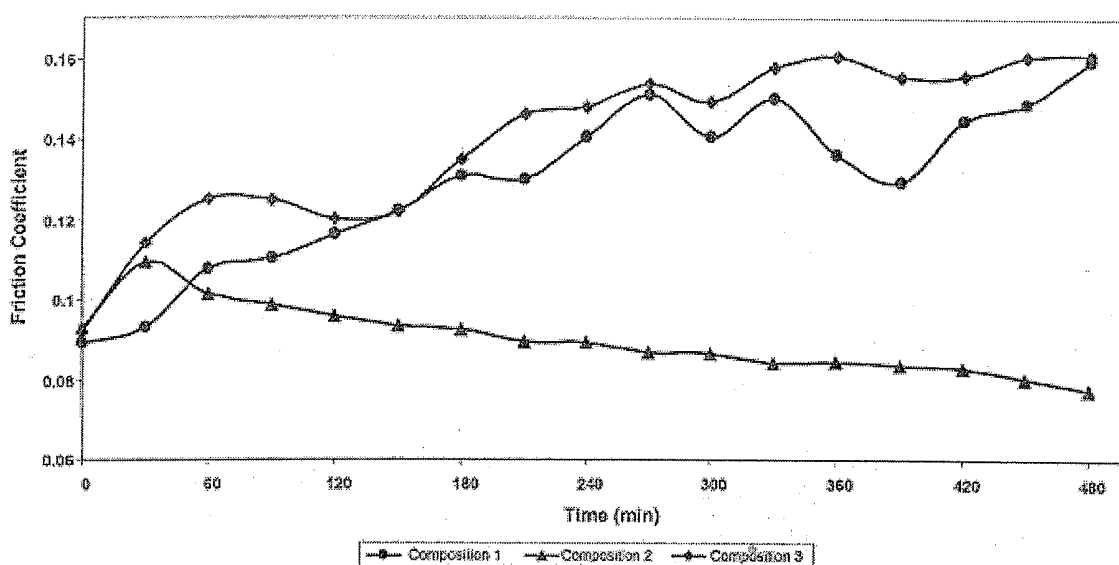


Table 1 (Friction Coefficient)

Time (min)	Comp.1	Comp.2	Comp.3	Comp.2% Improvement	Comp.3% Improvement
0	0.0895	0.0933	0.0920	-4.25	-2.79
30	0.0933	0.1094	0.1141	-17.26	-22.29
60	0.1077	0.1014	0.1253	5.85	-16.34
90	0.1105	0.0988	0.1249	10.59	-13.03
120	0.1164	0.0958	0.1203	17.70	-3.35
150	0.1222	0.0936	0.1218	29.31	0.32
180	0.1310	0.0926	0.1351	28.77	-3.13
210	0.1300	0.0896	0.1463	31.08	-12.54
240	0.1406	0.0892	0.1481	36.56	-5.33
270	0.1509	0.0871	0.1535	42.28	-1.72
300	0.1406	0.0868	0.1494	38.26	-6.26
330	0.1500	0.0842	0.1578	43.87	-5.20

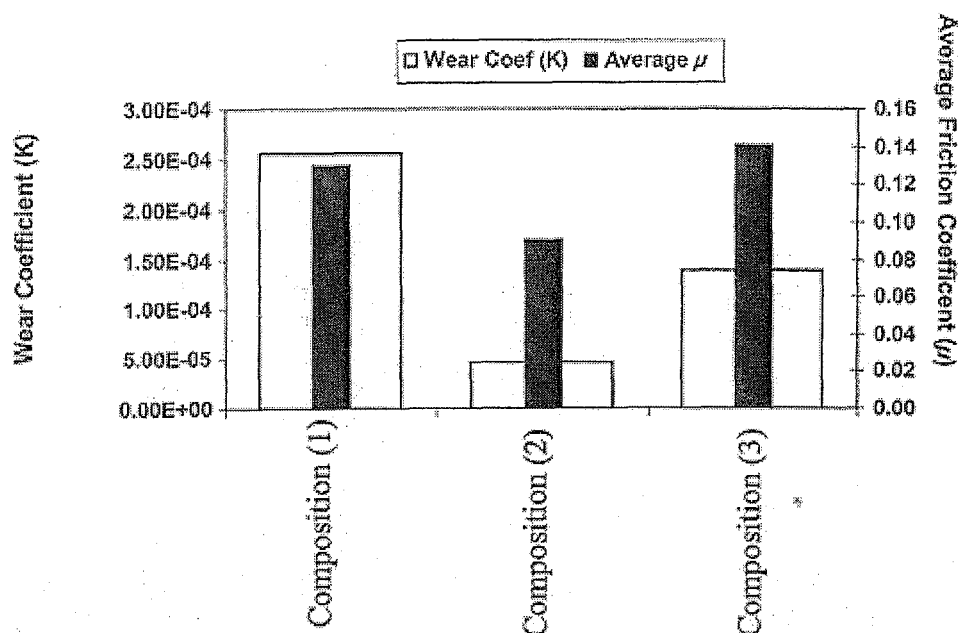
Table continued

Time (min)	Comp.1	Comp.2	Comp.3	Comp.2% Improvement	Comp.3% Improvement
360	0.1361	0.0847	0.1606	37.77	-18.00
390	0.1293	0.0836	0.1555	35.34	-20.26
420	0.1448	0.0833	0.1558	42.47	-20.49
450	0.1488	0.0805	0.1606	45.90	-7.93
480	0.1595	0.0777	0.1610	51.29	-0.94

Note: % Improvement is measured relative to Composition 1

[0069] From Graph 2 below, it can be seen that the alumina plate suffers significantly lower wear when lubricated with Composition 2, containing the trinuclear organo-molybdenum compound, than when lubricated with lubricating Composition 1 or 3.

Graph 2



[0070] A comparison of friction coefficient for Compositions 2, 4 and 5 is set out in Table 2 and Graph 3.

[0071] From Graph 3 it can be seen that Composition 5 exhibits a lower friction coefficient than Composition 4. Although, addition of ZDDP to the trinuclear organo-molybdenum containing composition, Composition 2, has a negative impact on the friction reduction associated with the trinuclear molybdenum compound, the above graph shows that the primary ZDDP of Composition 5 has a less detrimental effect on the friction coefficient than secondary ZDDP of Composition 4.

Graph 3

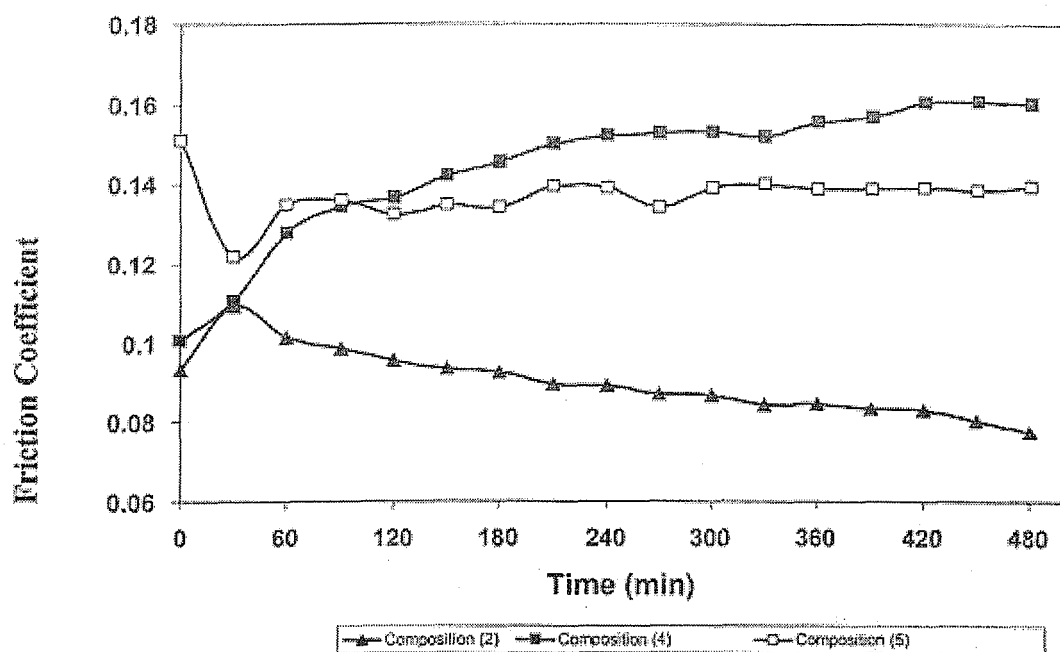


Table 2 (Friction Coefficient)

Time (min)	Comp. 2	Comp. 4	Comp.5
0	0.0933	0.1006	0.1512
30	0.1094	0.1105	0.1218
60	0.1014	0.1279	0.1348
90	0.0988	0.1347	0.1362
120	0.0958	0.1366	0.1325
150	0.0936	0.1422	0.1348
180	0.0926	0.1455	0.1344
210	0.0896	0.1501	0.1395
240	0.0892	0.1524	0.1397
270	0.0871	0.1529	0.1344
300	0.0868	0.1531	0.1392
330	0.0842	0.1520	0.1400
360	0.0847	0.1557	0.1388
390	0.0836	0.1568	0.1389
420	0.0833	0.1604	0.1391
450	0.0805	0.1607	0.1387
480	0.0777	0.1603	0.1396

Example 2 BS EN1452 pin on a BS EN31 plate

[0072] A comparison of friction coefficient for Compositions 1, 2 and 3 is set out in Table 3 and Graph 4. A comparison of wear coefficient for Compositions 1, 2 and 3 is set out in Graph 5.

[0073] From Table 3 and Graph 4 below, it can be seen that composition 2, comprising the trinuclear organo-molybdenum compound, results in significantly lower friction coefficient than lubricant Compositions 1 or 3. The percentage improvement figures in Table 3 illustrate that Composition 2 provides an increasingly better friction performance when compared with either Composition 1 or 3, as the test proceeds. Graph 4 and Table 3 also illustrates that Composition 3, comprising dinuclear molybdenum actually exhibits coefficients of friction that are higher than Composition 1, with no molybdenum additive.

Graph 4

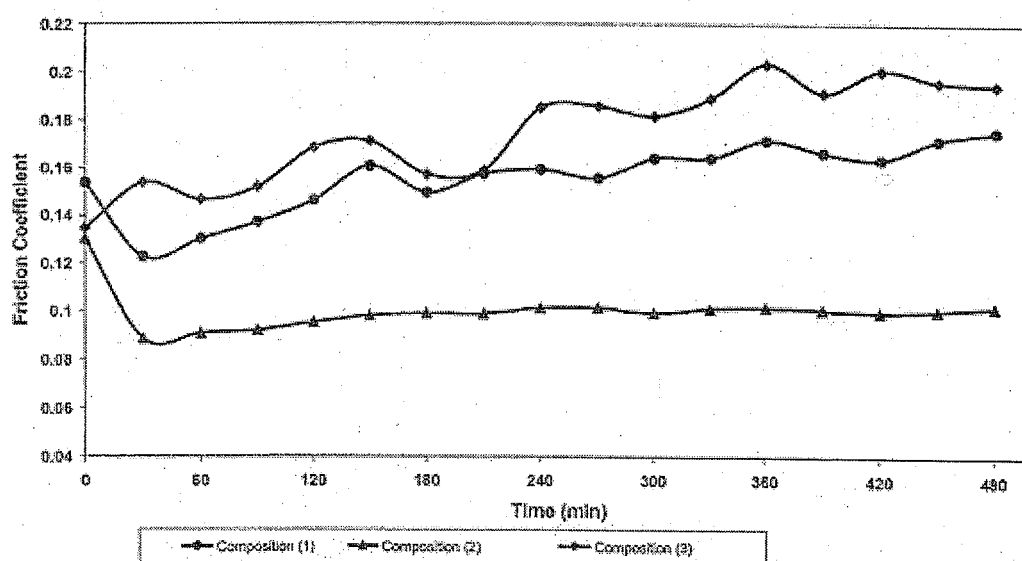


Table 3 (Friction Coefficient)

Time (min)	Comp. 1	Comp. 2	Comp.3	Comp. 2 % Improvement	Comp. 3 % Improvement
0	0.1537	0.1303	0.1437	6.51	6.51
30	0.1228	0.0888	0.1539	27.69	-25.33
60	0.1302	0.0909	0.1486	30.18	-14.13
90	0.1372	0.0921	0.1626	32.87	-18.51
120	0.1463	0.0953	0.1825	34.86	-24.74
150	0.1606	0.0980	0.1816	38.98	-13.08
180	0.1494	0.0990	0.1943	33.73	-30.05
210	0.1574	0.0988	0.1935	37.23	-22.94
240	0.1593	0.1012	0.1981	36.47	-24.36
270	0.1557	0.1013	0.1832	34.94	-17.66
300	0.1640	0.0992	0.1954	39.51	-19.15
330	0.1641	0.1010	0.1758	38.45	-7.13
360	0.1715	0.1015	0.2115	40.82	-23.32

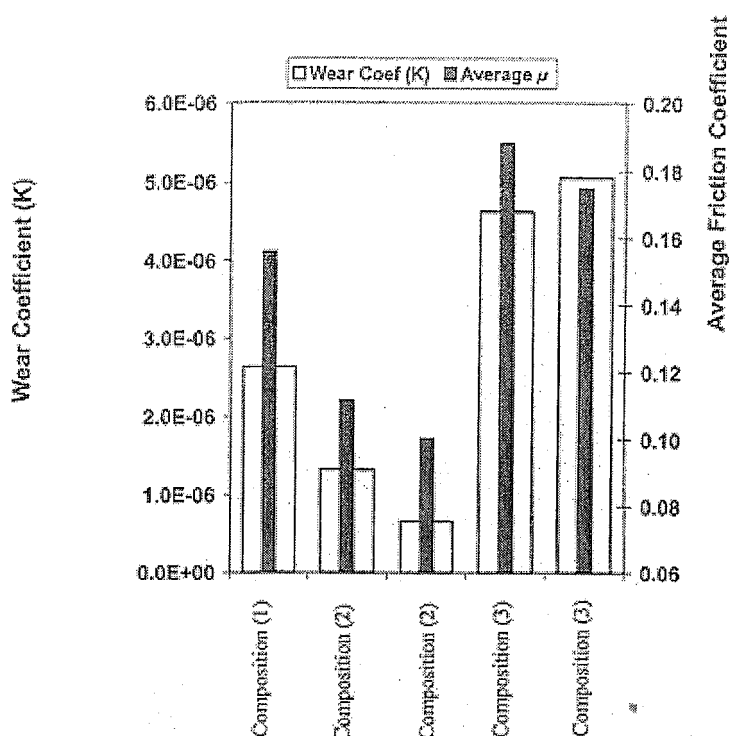
EP 1 624 044 A1

Table continued

Time (min)	Comp. 1	Comp. 2	Comp.3	Comp. 2 % Improvement	Comp. 3 % Improvement
390	0.1664	0.1006	0.2142	39.54	-28.73
420	0.1635	0.0995	0.2197	39.14	-34.37
450	0.1717	0.1003	0.2184	41.58	-27.20
480	0.1752	0.1019	0.2183	41.84	-24.60
Note: % Improvement is measured relative to Composition 1					

[0074] From Graph 5 below, it can be seen that the BS EN31 plate exhibits significantly less wear when lubricated with Composition 2 than with either of lubricating Compositions 1 or 3.

Graph 5



[0075] A comparison of friction coefficient for Compositions 2, 4 and 5 is set out in Table 4 and Graph 6,

[0076] From Table 4 and Graph 6 below, it can be seen that lubricating Composition 4 effects a greater reduction in friction coefficient than either of lubricating Compositions 2 or 5. Surprisingly, when lubricating a BS EN1452 pin on a BS EN31 plate addition of secondary ZDDP additive (Composition 4) to a lubricant containing trinuclear molybdenum improves the coefficient of friction. It is noted that addition of primary ZDDP (Composition 5) to the lubricant in place of secondary ZDDP has a detrimental effect of the coefficient of friction.

Graph 6

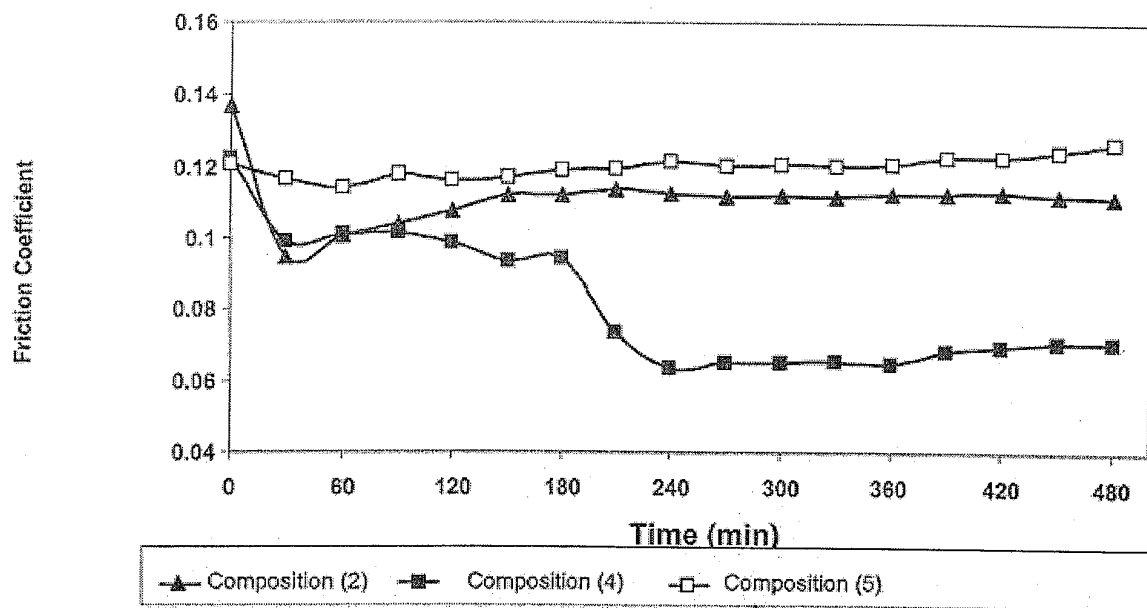


Table 4 (Friction Coefficient)

Time (min)	Comp. 2	Comp. 4	Comp. 5
0	0.1303	0.1225	0.1207
30	0.0888	0.0991	0.1170
60	0.0909	0.1013	0.1140
90	0.0921	0.1016	0.1177
120	0.0953	0.0988	0.1163
150	0.0980	0.0935	0.1169
180	0.0990	0.0942	0.1189
210	0.0988	0.0737	0.1196
240	0.1012	0.0637	0.1213
270	0.1013	0.0650	0.1204
300	0.0992	0.0650	0.1208
330	0.1010	0.0656	0.1204
360	0.1015	0.0648	0.1206
390	0.1006	0.0682	0.1227
420	0.0995	0.0698	0.1227
450	0.1003	0.0707	0.1245
480	0.1019	0.0710	0.1267

Claims

1. A method of lubricating an aluminum alloy surface, which comprises supplying to said surface a lubricating oil composition comprising an oil of lubricating viscosity and an oil-soluble trinuclear organo-molybdenum compound.
2. A method according to claim 1, 2 or 3, wherein the aluminum alloy is an aluminum-silicon alloy, having a hardness of 100-150Hv and a density of 2.0-3.0 gcm⁻³.
3. A method according to claim 1 or 2, wherein the lubricating oil composition further comprises primary ZDDP.
4. A method according to claim 1, 2 or 3, wherein the aluminum alloy surface is that of a component part of an internal combustion engine, and the lubricating oil composition is supplied to the engine.
5. A method of providing lubrication between two ferrous surfaces, one of the ferrous surfaces comprising a chromium containing steel alloy conforming to British Standard BS EN31, and the other ferrous surface comprising an iron alloy conforming to British Standard BS EN1452, which method comprises supplying to said surfaces a lubricating composition comprising an oil of lubricating viscosity, preferably in a major amount, and an oil-soluble trinuclear organo-molybdenum compound.
6. A method according to claim 5, wherein the lubricating oil composition further comprises a secondary ZDDP.
7. A method according to any one of the preceding claims, wherein the lubricating oil composition further comprises on or more additional additives selected from the group consisting of ashless dispersants, metal detergents, corrosion inhibitors, metal dihydrocarbyl dithiophosphates, antioxidants, pour point depressants, anti-foaming agents, additional friction modifiers, antiwear agents and viscosity modifiers.
8. A method according to any one of the preceding claims, wherein the trinuclear organo-molybdenum compound is a trinuclear dithiocarbamate compound.
9. An internal combustion engine having one or more component parts made from an aluminum alloy, and contained in a reservoir in the engine, a lubricating oil composition for lubricating said part comprising an oil of lubricating viscosity, in a major amount, and an oil-soluble, trinuclear organo-molybdenum compound.
10. An internal combustion engine having a component part made from a chromium containing ferrous alloy conforming with British Standard BS EN31 adjacent a component part made from a cast iron alloy conforming with British Standard BS EN1452, both component parts being contained in a reservoir in the engine, a lubricating oil composition for lubricating said parts comprising an oil of lubricating viscosity, in a major amount, and an oil-soluble, trinuclear organo-molybdenum compound.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 10 5029

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	WO 98/26030 A (EXXON RESEARCH ENGINEERING CO ; EXXON CHEMICAL PATENTS INC (US)) 18 June 1998 (1998-06-18) * page 1, paragraph 3 * * page 2, paragraph 3 - page 6, paragraph 2 * * page 9, paragraph 3 * * examples *	1-10	C10M159/18 C10M163/00
Y	----- VOONG M, NEVILLE A, CASTLE R: "The compatibility of crankcase lubricant-material combinations in internal combustion engines" TRIBOLOGY LETTERS, vol. 15, no. 4, November 2003 (2003-11), pages 431-441, XP002307060 * page 432, paragraph 2 - paragraph 2.2; table 1 * -----	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C10M
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 15 July 2005	Examiner Keipert, O
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 10 5029

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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15-07-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9826030 A	18-06-1998	US 5888945 A	30-03-1999
		US 6358894 B1	19-03-2002
		AU 729795 B2	08-02-2001
		AU 6002498 A	03-07-1998
		BR 9713710 A	24-10-2000
		CA 2274706 A1	18-06-1998
		DE 69707714 D1	29-11-2001
		DE 69707714 T2	25-04-2002
		EP 0960178 A1	01-12-1999
		WO 9826030 A1	18-06-1998
		JP 2001515528 T	18-09-2001
		KR 2000057571 A	25-09-2000
		US 6232276 B1	15-05-2001
		US 6010987 A	04-01-2000
