PATENT APPLICATION

TITLE

Method of Lubricating an Internal Combustion Engine

FIELD OF INVENTION

The present invention relates to a method of lubricating an internal combustion engine comprising supplying to said engine a metal base dispersed in an organic medium. The metal base has a high solids content and a particle size of less than 1 μm.

BACKGROUND OF THE INVENTION

[0001] Lubricating compositions suitable for an internal combustion engine need to lubricate moving parts as well as operate at high temperature and pressures. Whilst the engine is operating, corrosive acids form during combustion along with sludge and other deposits. Typically, detergents such as sulphonates, salicylates or phenates have been employed to neutralize corrosive acids. The detergents often have a total base number (TBN) ranging from 10 to 500. Further conventional detergents deliver a limited TBN relative to treat rate. Therefore it would be advantageous to provide an internal combustion engine with a lubricant with at least one property selected from: providing a source of TBN capable of treating at a lower level, providing a source of TBN capable of neutralising corrosive acids formed during combustion of fuel, and providing a source of TBN capable of being stable in a lubricant. The present invention provides an internal combustion engine with a lubricant capable of imparting at least one of said properties.

[0002] GB 1,096,008 discloses a lubricating composition containing dispersed alkaline earth metal compounds prepared by milling. The alkaline earth metal compounds are oil-insoluble with a particle size of 1 to 30 microns and are dispersed from 20 to 80 weight percent of the lubricating composition. The alkaline earth metal compounds are a metal hydroxide or a mixture of metal hydroxides in combination with alkaline earth metal carboxylate of an alkanoic acid.

[0003] GB 1,034,970 discloses a process for preparing transparent colloidal dispersions in oil of a polyvalent metal carbonate in the presence of ammonium hydroxide.

SUMMARY OF THE INVENTION

[0004] The present invention in one embodiment provides a method of lubricating an internal combustion engine comprising supplying to said engine a dispersion, the dispersion comprising: (a) a metal base; (b) a surfactant; and (c) an organic medium in which the metal base is uniformly dispersed by physical processes, wherein the metal base has a mean average particle size of at least 10 nanometres to less than 1 μm; and the dispersion has a solids content of greater than 15 wt %.

[0005] In one embodiment the invention provides a lubricant composition comprising (i) a dispersion comprising: (a) a metal base; (b) a surfactant; and (c) an organic medium in which the metal base is uniformly dispersed by physical processes, wherein the metal base has a mean average particle size of at least 10 nanometres to less than 1 μm; and the dispersion has a solids content of greater than 15 wt %; (ii) an oil of lubricating viscosity; and (iii) other performance additives.

DETAILED DESCRIPTION OF THE INVENTION

[0006] The present invention provides a lubricating composition and a method of lubricating an internal combustion engine as disclosed above.

[0007] In one embodiment the invention is other than a water-containing emulsion.

[0008] As used herein the term "free of", as used in the specification and claims, defines the absence of a material except for the amount which is present as impurities, e.g., a trace amount or a non-effective amount. Typically in this embodiment, the amount present will be less than 0.05% or less than 0.005 wt % by weight of the dispersion.

[0009] In one embodiment the dispersion is substantially free of, to free of, a metal carboxylate, such as calcium acetate.

[0010] The dispersion may have a total base number (TBN) ranging from 20 to 2000, or from 200 to 1750, or from 400 to 1500, or from 600 to 1300.

[0011] In different embodiments the dispersion may be opaque or semi-translucent or translucent or transparent, or any gradation between such descriptions.

[0012] The dispersion may be prepared by physical processes, that is, by any one or more of various physical processes, i.e., physical processing steps. Examples of physical process include milling, grinding or crushing. Typically the milling process grinds the metal base to a mean average particle size of at least 10 nanometres to less than 1 μm. Milling processes include using a rotor stator mixer, a vertical bead mill, a horizontal bead mill, basket milling, ball mill, pearl milling or mixtures thereof. In one embodiment, the physical processes for preparing the dispersion comprise using a vertical or horizontal bead mill. In one embodiment the physical process is other than a chemical means, for example, one not requiring ammonium hydroxide.

[0013] In different embodiments the milling process may be carried out in a vertical or horizontal bead mill. Either bead mill processes cause the reduction of particle size of the metal base by high energy collisions of the metal base with at least one bead; and/or other metal base agglomerates, aggregates, solid particles; or mixtures thereof. The beads typically have a mean particle size and mass greater than the desired mean particle size of the metal base. In some instances the beads are a mixture of different mean particle size. The beads used in the grinding may be of materials known to those skilled in the art, such as metal ceramic, glass, stone, or composite materials.

[0014] The mill typically contains beads present at least 40 vol %, or at least 60 vol % of the mill. A range include for example 60 vol % to 95 vol %. A more detailed description of making the dispersion is disclosed in US Patent Application Number US05/010631.

Metal Base

[0015] The dispersion of the metal base comprises a mono- or di- or tri- or tetra- valent metal or a mixture thereof. Typically the metal of the metal base is a monovalent or divalent metal. In one embodiment the metal base is derived from a monovalent metal including lithium, potassium, sodium, copper, zinc, or mixtures thereof. In one embodiment the metal base is derived from a divalent

metal including magnesium, calcium, barium or mixtures thereof. The metal may also have multiple valence, e.g., mono- or di- or tri- valent with copper or iron as examples. In one embodiment the metal base is derived from a tetravalent metal including cerium. The metal base optionally contains water of hydration or crystallisation. In one embodiment the metal base is crystalline. In various embodiments the metal comprises calcium or magnesium.

[0016] The amount of metal base present in the dispersion, that is, the solids content, is greater than 15 wt % and may range from 17 wt % to 90 wt %, or from 25 wt % to 80 wt %, or from 35 wt % to 70 wt %, or from 40 wt % to 65 wt % of the dispersion. This amount is determined on the basis of the original dispersion and does not include any additional diluent into which the dispersion may be subsequently admixed to form, for instance, a fully formulated lubricating composition, nor does it include solids or non-volatile components from other sources.

[0017] The metal base is typically in the form of a solid and is not appreciably soluble in the organic medium. In several embodiments the metal base has a mean particle size in the dispersion ranging from 20 nanometres to of less than 1 μm, or 30 nanometres to 0.7 μm, or 50 nanometres to 0.4 μm, or 80 nanometres to 0.3 μm.

[0018] The metal base generally comprises at least one of oxides, hydroxides or carbonates. Examples of a suitable metal base include sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, potassium hydroxide, sodium hydroxide, anhydrous lithium hydroxide, lithium hydroxide monohydrate, magnesium hydroxide, calcium hydroxide, lithium carbonate, calcium carbonate, magnesium carbonate, calcium oxide, magnesium oxide, lithium oxide, cerium oxide, iron oxide or mixtures thereof. In one embodiment of the invention the metal base is present in a mixture, for instance, dolmitic lime, which is commercially available. In several embodiments the metal base is calcium hydroxide or calcium oxide.

Surfactant

[0019] The surfactant includes an ionic (cationic or anionic) or non-ionic compound. Generally, the surfactant stabilises the dispersion of the metal base in the organic medium.

[0020] Suitable surfactant compounds include those with a hydrophilic lipophilic balance (HLB) ranging from 1 to 40, or 1 to 20, or 1 to 18, or 2 to 16, or 2.5 to 15. In several embodiments the HLB may be 11 to 14, or less than 10 such as 1 to 8, or 2.5 to 6. Those skilled in the art will appreciate that combinations of surfactants may be used with individual HLB values outside of these ranges, provided that the composition of a final surfactant blend is within these ranges. When the surfactant has an available acidic group, the surfactant may become the metal salt of the acidic group and where the metal is derived from the metal base.

[0021] Examples of surfactants suitable for the invention are disclosed in McCutcheon's Emulsifiers and Detergents, 1993, North American & International Edition. Generic examples include alkanolamides, alkylarylsulphonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units (e.g., Pluronic™), carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, glycerol esters, glycol esters, imidazoline derivatives, phenates, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulphonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkyl phenols, sorbitan derivatives, sucrose esters and derivatives, sulphates or alcohols or ethoxylated alcohols or fatty esters, polyisobutylene succinicimide and derivatives.

[0022] In one embodiment the surfactant comprises polyesters as defined in column 2, line 44 to column 3, line 39 of US 3,778,287. Examples of suitable polyester surfactants are prepared in US 3,778,287 as disclosed in Polyester Examples A to F (including salts thereof).

[0023] In one embodiment the surfactant is a hydrocarbyl substituted aryl sulphonic acid (or sulphonate) of an alkali metal, alkaline earth metal or mixtures thereof. The aryl group of the aryl sulphonic acid may be phenyl or naphthyl. In

one embodiment the hydrocarbyl substituted aryl sulphonic acid comprises alkyl substituted benzene sulphonic acid.

[0024] The hydrocarbyl (especially an alkyl) group typically contains 8 to 30, or 10 to 26, or 10 to 15 carbon atoms. In one embodiment the surfactant is a mixture of C_{10} to C_{15} alkylbenzene sulphonic acids. Examples of sulphonates include dodecyl and tridecyl benzene sulfonates or condensed naphthalenes or petroleum sulfonates, as well as sulphosuccinates and derivatives.

[0025] In one embodiment the surfactant is in the form of a neutral or over-based surfactant, typically salted with an alkali or alkaline earth metal. The alkali metal includes lithium, potassium or sodium; and the alkaline earth metal includes calcium or magnesium. In one embodiment the alkali metal is sodium. In one embodiment the alkaline earth metal is calcium.

[0026] In one embodiment the surfactant is a derivative of a polyolefin. Typical examples of a polyolefin include polyisobutene; polypropylene; polyethylene; a copolymer derived from isobutene and butadiene; a copolymer derived from isobutene and isoprene; or mixtures thereof.

[0027] Typically the derivative of a polyolefin comprises a polyolefin-substituted acylating agent optionally further reacted to form an ester and/or aminoester. The acylating agent may be a compound with one or more acid functional groups, such as a carboxylic acid or anhydride thereof. Examples of an acylating agent include an alpha, beta-unsaturated mono- or polycarboxylic acid, anhydride ester or derivative thereof. Examples of an acylating agent thus include (meth) acrylic acid, methyl (meth) acrylate, maleic acid or anhydride, fumaric acid, itaconic acid or anhydride, or mixtures thereof, each of which may typically be in the form of the saturated materials (e.g. succinic anhydride) after reaction with the polyolefin.

[0028] In one embodiment the polyolefin is a derivative of polyisobutene with a number average molecular weight of at least 250, 300, 500, 600, 700, or 800, to 5000 or more, often up to 3000, 2500, 1600, 1300, or 1200. Typically, less than 5% by weight of the polyisobutylene used to make the derivative molecules have $\overline{Mn}$ less than 250, more often the polyisobutylene used to make the derivative has $\overline{Mn}$ of at least 800. The polyisobutylene used to make the derivative preferably

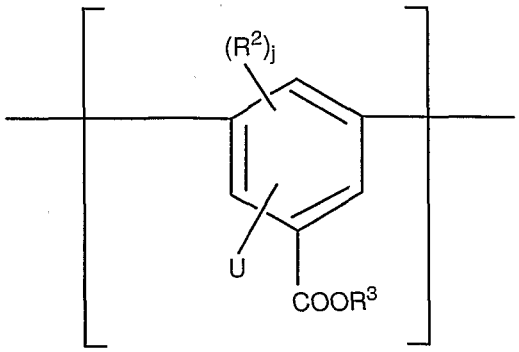
contains at least 30% terminal vinylidene groups, more often at least 60% or at least 75% or 85% terminal vinylidene groups. The polyisobutylene used to make the derivative may have a polydispersity, $\overline{Mw}/\overline{Mn}$, greater than 5, more often from 6 to 20.

[0029] In various embodiments, the polyisobutene is substituted with succinic anhydride, the polyisobutene substituent having a number average molecular weight ranging from 1,500 to 3,000, or 1,800 to 2,300, or 700 to 1700, or 800 to 1000. The ratio of succinic groups per equivalent weight of the polyisobutene typically ranges from 1.3 to 2.5, or 1.7 to 2.1, or 1.0 to 1.3, or 1.0 to 1.2.

[0030] In one embodiment the surfactant is polyisobutenyl-dihydro-2,5-furandione ester with pentaerythritol or mixtures thereof. In one embodiment the surfactant is a polyisobutylene succinic anhydride derivative such as a polyisobutylene succinimide or derivatives thereof. In one embodiment the surfactant is substantially free to free of a basic nitrogen.

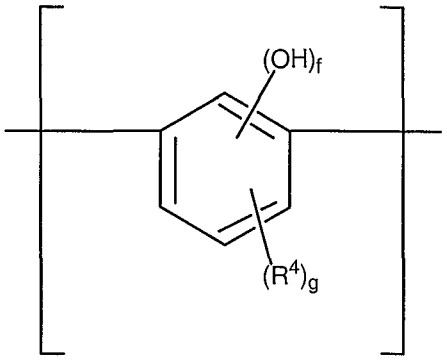
[0031] Other typical derivatives of polyisobutylene succinic anhydirdes include hydrolysed succinic anhydrides, esters or diacids. Polyisobutylene succan derivatives are preferred to make the metal base dispersions. A large group of polyisobutylene succinic anhydride derivatives are taught in US 4,708,753, and US 4,234,435.

[0032] In another embodiment the surfactant comprises a salixarene (or salixarate if in the form of a metal salt). The salixarene is defined as an organic substrate of a salixarate. The salixarene may be represented by a substantially linear compound comprising at least one unit of the formulae (I) or (II):



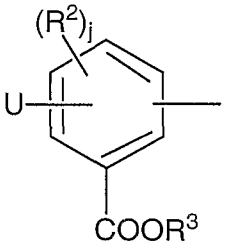
(I)

or

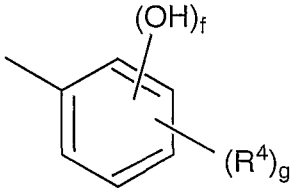


(II)

each end of the compound having a terminal group of formulae (III) or (IV):



(III)



(IV)

such groups being linked by divalent bridging groups, which may be the same or different for each linkage; wherein f is 1, 2 or 3, in one aspect 1 or 2; R^2 is hydroxyl or a hydrocarbyl group and j is 0, 1, or 2; R^3 is hydrogen or a hydrocarbyl group; R^4 is a hydrocarbyl group or a substituted hydrocarbyl group; g is 1, 2 or 3, provided at least one R^4 group contains 8 or more carbon atoms; and wherein the compound on average contains at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is about 0.1:1 to about 2:1.

[0033] The U group in formulae (I) and (III) may be an –OH or an $–NH_2$ or $-NHR^1$ or $–N(R^1)_2$ group located in one or more positions ortho, meta, or para to the $-COOR^3$ group. R^1 is a hydrocarbyl group containing 1 to 5 carbon atoms.When the U group comprises a –OH group, formulae (I) and (III) are derived from 2-hydroxybenzoic acid (often called salicylic acid), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid or mixtures thereof. When U is a $–NH_2$ group, formulae (I) and (III) are derived from 2-aminobenzoic acid (often

called anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic acid or mixtures thereof.

[0034] The divalent bridging group, which may be the same or different in each occurrence, includes an alkylene or methylene bridge such as $-CH_2-$ or –CH(R)- and an ether bridge such as $-CH_2OCH_2-$ or –CH(R)OCH(R)- where R is an alkyl group having 1 to 5 carbon atoms and where the methylene and ether bridges are derived from formaldehyde or an aldehyde having 2 to 6 carbon atoms.

[0035] Often the terminal group of formulae (III) or (IV) further contains 1 or 2 hydroxymethyl groups ortho to a hydroxy group. In one embodiment of the invention hydroxymethyl groups are present. In one embodiment of the invention hydroxymethyl groups are not present. A more detailed description of salixarene and salixarate chemistry is disclosed in EP 1 419 226 B1, including methods of preparation as defined in Examples 1 to 23 (page 11, line 42 to page 13, line 47).

[0036] In one embodiment the surfactant is substantially free of, to free of, a fatty acid or derivatives thereof, such as esters. In one embodiment the surfactant is other than a fatty acid or derivatives thereof.

[0037] In one embodiment the surfactant comprises at least of hydrocarbyl substituted aryl sulphonic acids, derivatives of polyolefins, polyesters or salixarenes (or salixarates).

[0038] In different embodiments the surfactant is substantially free of, to free of, phospholipids, (such as lecithin) and/or amino acids (such as sarcosines).

[0039] In one embodiment the surfactant has a molecular weight of less than 1000, in another embodiment less than 950, for example, 250, 300, 500, 600, 700, or 800.

[0040] The amount of surfactant and metal base in the dispersion may vary as is shown in Table 1, the balance being the organic medium and optionally water. In one embodiment the amount of oil present in the dispersion varies from 25 wt % to 55 wt %.

Table 1

	Embodiments (wt % of dispersion)			
Additive	1	2	3	4
Metal Base	17-90	25-80	35-70	40-65
Surfactant	0.01-30	1-30	2-30	5-25

Organic Medium

[0041] The organic medium may comprise an oil of lubricating viscosity, a liquid fuel, a hydrocarbon solvent or mixtures thereof. Typically the organic solvent comprises an oil of lubricating viscosity.

[0042] Optionally the organic medium contains water, typically up to 1 wt %, or 2 wt % or 3 wt % of the dispersion. In different embodiments the organic medium is substantially free of, to free of, water.

Oils of Lubricating Viscosity

[0043] In one embodiment the organic medium comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0044] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0045] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0046] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0047] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils

of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[0048] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0049] Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

[0050] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content $\leq$0.03 wt %, and $\geq$90 wt % saturates, viscosity index 80-120); Group III (sulphur content $\leq$0.03 wt %, and $\geq$90 wt % saturates, viscosity index $\geq$120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil and mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV oil and mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group I, Group II, Group III oil or mixtures thereof.

[0051] In an alternative embodiment the organic medium comprises a liquid fuel. The liquid fuel is useful in fueling an internal combustion engine or open flame combustion system. The liquid fuel is normally a liquid at ambient conditions. The liquid fuel includes a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel may be a petroleum distillate such as a

gasoline as defined by ASTM (American Society for Testing and Materials) specification D4814 or a diesel fuel as defined by ASTM specification D975. In an embodiment the liquid fuel is a gasoline, and in another embodiment the liquid fuel is a leaded gasoline, or a nonleaded gasoline. In another embodiment the liquid fuel is a diesel fuel. The hydrocarbon fuel includes a hydrocarbon prepared by a gas to liquid process for example hydrocarbons prepared by a process such as the Fischer-Tropsch process. The nonhydrocarbon fuel includes an oxygen containing composition (often referred to as an oxygenate), an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof. The nonhydrocarbon fuel includes methanol, ethanol, methyl t-butyl ether, methyl ethyl ketone, transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane. Mixtures of hydrocarbon and nonhydrocarbon fuels include gasoline and methanol and/or ethanol, diesel fuel and ethanol, and diesel fuel and a transesterified plant oil such as rapeseed methyl ester. In one embodiment the liquid fuel is a nonhydrocarbon fuel or a mixture thereof.

[0052] The dispersion may be used as a sole additive for a lubricant composition lubricating the internal combustion engine. In one embodiment the dispersion is used as one additive in combination with other performance additives to provide a lubricant composition lubricating the internal combustion engine. In one embodiment the invention provides a lubricant composition comprising (i) a dispersion comprising: (a) a metal base; (b) a surfactant; and (c) an organic medium in which the metal base is dispersed; (ii) an oil of lubricating viscosity; and (iii) other performance additives.

[0053] The lubricant composition may thus comprise an oil of lubricating viscosity as defined above, in addition to the amount which may be present as the organic medium of the dispersion.

Other Performance Additives

[0054] The lubricant composition optionally comprises other performance additives. The other performance additives comprise at least one of metal deactivators, detergents, dispersants, viscosity modifiers, friction modifiers, corrosion inhibitors, dispersant viscosity modifiers, extreme pressure agents,

antiscuffing agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

Dispersants

[0055] Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant. Dispersants also include polymeric dispersants. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in the range 350 to 5000, or 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance in US Patent 4,234,435. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0056] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene succinimide with number average molecular weight in the range 350 to 5000, or 500 to 3000. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0057] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc. The polyisobutylene succinimide complex with zinc may be used alone or in combination.

[0058] Another class of ashless dispersant is Mannich bases. Mannich dispersants are the reaction products of alkyl phenols with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

[0059] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron sources such as boric acid or borates, urea, thiourea, dimercaptothiadiazoles, carbon disul-

phide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

Detergents

[0060] The lubricant composition optionally further comprises neutral or overbased detergents. Suitable detergent substrates include sulphonates, salixarates, salicylates, carboxylates, phosphorus acid salts, mono- and/or di- thiophosphoric acid salts, phenates including alkyl phenates and sulphur coupled alkyl phenates, or saligenins.

[0061] In different embodiments, the lubricant composition further comprises at least one of sulphonates and phenates. When present, the detergents are typically overbased. The ratio of TBN delivered by the dispersion to that delivered by the detergent may range from 1:99 to 99:1, or 15:85 to 85:15.

Antioxidant

[0062] Antioxidant compounds are known and include an amine antioxidant (such as an alkylated diphenylamine), a hindered phenol, a molybdenum dithiocarbamate, and mixtures thereof. Antioxidant compounds may be used alone or in combination.

[0063] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol 2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0064] Suitable examples of molybdenum dithiocarbamates which may be used as an antioxidant include commercial materials sold under the trade names such as Vanlube 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165 and S-600 from Asahi Denka Kogyo K. K and mixtures thereof.

Viscosity Modifiers

[0065] Viscosity modifiers include styrene-butadiene rubbers, ethylene-propylene copolymers, hydrogenated styrene-isoprene polymers, hydrogenated radical isoprene polymers, poly(meth)acrylate acid esters, polyalkyl styrenes, polyolefins, polyalkylmethacrylates and esters of maleic anhydride-styrene copolymers, or mixtures thereof. In one embodiment the viscosity modifier (or polymeric thickener) is a poly(meth)acrylate.

Antiwear Agent

[0066] The lubricant composition optionally further comprises at least one antiwear agent. Examples of suitable antiwear agents include a sulphurised olefin, sulphur-containing ashless anti-wear additives, metal dihydrocarbyldi-thiophosphates (such as zinc dialkyldithiophosphates), thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disul-phides.

[0067] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamic acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulphide and an unsaturated compound. Generally, the reaction occurs at a temperature from 25 °C to125 °C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0068] Examples of suitable olefins that may be sulphurised to form an the sulphurised olefin include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester such as butyl(meth)acrylate.

[0069] Another class of sulphurised olefin includes fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and

typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and/or ester are mixed with olefins.

[0070] In an alternative embodiment, the ashless antiwear agent may be a monoester of a polyol and an aliphatic carboxylic acid, often an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid is in the form of a mixture with a sunflower oil or the like, which may be present in the friction modifier mixture from 5 to 95, in several embodiments from 10 to 90, or 20 to 85, or 20 to 80 weight percent of said mixture. The aliphatic carboxylic acids (especially a monocarboxylic acid) which form the esters are those acids typically containing 12 to 24 or 14 to 20 carbon atoms. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0071] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol. Often the polyol is diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol or dipentaerythritol.

[0072] The commercially available monoester known as "glycerol monooleate" is believed to include 60 $\pm$ 5 percent by weight of the chemical species glycerol monooleate, along with 35 $\pm$ 5 percent glycerol dioleate, and less than 5 percent trioleate and oleic acid.

Antiscuffing Agent

[0073] The lubricant composition may also contain an antiscuffing agent. Antiscuffing agent compounds are believed to decrease adhesive wear and are often sulphur containing compounds. Typically the sulphur containing compounds include organic sulphides and polysulphides, such as dibenzyldisulphide, bis–(chlorobenzyl) disulphide, dibutyl tetrasulphide, di-tertiary butyl

polysulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, sulphurised Diels-Alder adducts, alkyl sulphenyl N'N-dialkyl dithiocarbamates, the reaction product of polyamines with polybasic acid esters, chlorobutyl esters of 2,3-dibromopropoxyisobutyric acid, acetoxymethyl esters of dialkyl dithiocarbamic acid and acyloxyalkyl ethers of xanthogenic acids and mixtures thereof.

Extreme Pressure Agents

[0074] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulphides and polysulphides such as dibenzyldisulphide, bis--(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; the zinc salts of a phosphorodithioic acid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

[0075] Other performance additives such as corrosion inhibitors including octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine; metal deactivators including derivatives of benzotriazoles, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-

styrene, polymethacrylates, polyacrylates or polyacrylamides; and friction modifiers including fatty acid derivatives such as amines, esters, epoxides, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids may also be used in the lubricant composition.

Industrial Application

[0076] The dispersion is useful for an internal combustion engine, for example a diesel fuelled engine, a gasoline fuelled engine, a natural gas fuelled engine or a mixed gasoline/alcohol fuelled engine. In one embodiment the internal combustion engine is a diesel fuelled engine and in another embodiment a gasoline fuelled engine.

[0077] The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, automobile engines and truck engines.

[0078] In several embodiments a suitable lubricating composition comprises additives present on an actives basis in ranges as shown in Table 2.

Table 2

	Embodiments (wt % of lubricant composition)			
Additive	1	2	3	4
Dispersion	0.01-50	0.1-25	0.5-10	0.75-5
Other Performance Additives	0-30	0.01-25	0.1-20	0.5-15
Oil of Lubricating Viscosity	20-99.99	50-99.89	70-99.4	80-98.5

[0079] In one embodiment, the invention provides a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the dispersion as described herein. The use of the dispersion in an internal combustion engine may impart one or more properties such as providing TBN and providing acid neutralisation.

[0080] The following examples provide an illustration of the invention. These examples are non exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

Preparative Examples of Dispersions

[0081] A series of dispersions containing a metal base, an organic medium and a surfactant are prepared from a slurry comprising 40 wt % to 50 wt % of the metal base, 6 wt % to 15 wt % of a surfactant and the remained a hydrocarbon fluid, typically solvent neutral 100 mineral oil. 2 kg to 5 tonnes of the slurry is milled in a horizontal bead mill with a milling chamber of suitable size appropriate for the scale of the operation. The bead size filling the chamber (typically 65 vol. %) is typically in the range 0.7 mm to 0.1 mm diameter (e.g. 0.3 mm +/- 0.05 mm beads). After a suitable amount of milling, typically 4 to 20 minutes residence time (i.e. the actual time the dispersion spends in the mill) the required particle size is achieved (i.e. ≤1 μm) as determined by Coulter® LS230 Particle Size Analyser. The dispersion is easy to pour and stable for several weeks between -20 °C and + 60°C, showing no tendency to stratify or to form a gel. The preparative examples prepared are shown in Table 4.

[0082] Preparative Example 15 is prepared by taking the dispersion of Preparative Example 14 and continuing the processing using 0.05 mm beads and with a residence time of 30-60 minutes. Preparative Example 15 has 25 % of particles of < 100 nm.

Table 4

			Surfactant		Metal Base				
Prep Ex	**Bead Size (mm)**	**Res. Time**	**Type**	**Wt %**	**Type**	**Wt %**	**Disp. TBN**	**% <1 µm**	**Mean µm**
1	0.3	9	A	6	CaO	44	880	85	0.4
2	0.3	9	B	10	$Ca(OH)_2$	50	760	96.4	0.3
3	0.3	8	C	10	$Ca(OH)_2$	50	760	100	0.2
4	0.3	6	D	10	$Ca(OH)_2$	50	760	96.9	0.3
5	0.3	7	A	10	$Ca(OH)_2$	50	760	94.8	0.4
6	0.3	6	E	10	$Ca(OH)_2$	50	760	97.4	0.3
7	0.3	6	F	10	$Ca(OH)_2$	50	760	92.6	0.4
8	0.3	7	G	10	$Ca(OH)_2$	50	760	97.9	0.3
9	0.3	7	H	10	$Ca(OH)_2$	50	760	100	0.2
10	0.3	7	J	10	$Ca(OH)_2$	50	760	100	0.3
11	0.3	10	B	10	$CaCO_3$	50	760	82.9	0.6
12	0.3	10	A	10	$CaCO_3$	50	760	84.7	0.6
13	0.1	30	B	15	$Ca(OH)_2$	50	760	100	0.2
14	0.1	19-60	D	15	MgO	50	1300	100	0.2
15	0.05	30-60	D	15	MgO	50	1300	100	0.1

Footnote to Table 4

Prep Ex is Preparative Example;

Res. Time is the residence time dispersion is prepared in mill;

Disp. TBN is the TBN of the dispersion (mg KOH/g);

Mean is mean particle size;

Surfactant A is an alkyl benzene sulphonic acid;

Surfactants B and C are polyisobutylene succinimides prepared from triethylene tetramine and polyethylene amine, respectively;

Surfactant D is an ester prepared from polyisobutylene maleic anhydride reacted with 2-(dimethylamino)ethanol.

Surfactants E and F are Examples 7 and 5 respectively from EP1 419 226;

Surfactant G is a phenate; and

Surfactants H and J are Polyester A (as disclosed in US 3,778,287, column 3, lines 55 to 65) and Polyester B (as disclosed in US 3,778,287, column 3, line 69 to column 4, line 7) respectively.

Engine Oil Lubricants 1 to 120

[0083] A series of SAE 30 (Engine Oil Examples 1 to 60) and SAE 15W-40 (Engine Oil Examples 61 to 120) engine oil lubricants are prepared by blending into each, the product of Preparative Examples 1 to 15. The engine lubricants

further contain a conventional amount of zinc dialkyldithiophosphate, succinimide dispersant and optionally an amount of a sulphonate detergent, as indicated. The engine lubricants are formulated to have a TBN of 11.4 mg KOH/g. Typically the engine lubricants prepared with dispersions with particle sizes below about 200 or below about 300 nm are semi-translucent to translucent. The engine oils prepared are presented in Table 5.

Table 5

Engine Oil Lubricant Example	Engine Oil Lubricant Grade	Preparative Example present	% of TBN from Prep Ex	% of TBN from Sulphonate Detergent
1-15	SAE 30	1-15	25	75
16-30		1-15	50	50
31-45		1-15	75	25
46-60		1-15	100	0
61-75	15W-40	1-15	25	75
76-90		1-15	50	50
91-105		1-15	75	25
106-120		1-15	100	0

[0084] A comparative engine oil lubricant is prepared containing conventional amounts of sulphonate and phenate detergent instead of the dispersion of the present invention. The TBN of the comparative engine lubricant is formulated to be 11.4.

[0085] The engine lubricants are then evaluated for oxidative stability using the Panel Coker test with panels splashed and cooked in alternate cycles whilst held at 310 °C for 4 hours. The panels are removed and visually evaluated and graded on a de-merit scale of 1 to 10. The average Demerit Rating is based on 1 average rating to one significant number based on Examples tested. Typically, better results are obtained for samples that have a lower demerit rating. The results obtained are:

Table 6

SAE 30			15W-40		
Examples (from Prep Ex)	Metal Base	Average Demerit Rating	Examples (from Prep Ex)	Metal Base	Average Demerit Rating
Comparative	-	3	Comparative	-	6
Engine Oil 1	CaO	1	Engine Oil 61	CaO	4
Engine Oil 5	$Ca(OH)_2$	2	Engine Oil 65	$Ca(OH)_2$	5
Engine Oil 12	$CaCO_3$	1	Engine Oil 72	$CaCO_3$	4

Marine Lubricants 1 to 120

[0086] Marine diesel trunk piston engine lubricants are prepared with a TBN of 40 and 70 are each prepared using Preparative Examples 1 to 15. The marine lubricants contain reduced amounts of over-based calcium sulphonate and calcium phenate detergents compared with conventional marine lubricants.

[0087] An example of the marine lubricant formulation contains (i) 5 wt % of calcium hydroxide dispersion (from Preparative Examples 2 to 10 or 13), (ii) approximately 1 wt % of succinimide dispersant, and (iii) a detergent package of calcium phenate and calcium sulphonate (combined 3.5 wt %), with the balance of base oil to total 100 % by weight. The marine lubricants are studied over 12 weeks for storage stability at ambient temperature and at 60 °C. All of the marine lubricants are stable after 3 months.

[0088] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

(ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphoxy);

(iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0089] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0090] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be

understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

What is claimed is:

1. A method of lubricating an internal combustion engine comprising supplying to said engine a dispersion, the dispersion comprising: (a) a metal base; (b) a surfactant; and (c) an organic medium in which the metal base is uniformly dispersed by physical processes, wherein the metal base has a mean average particle size of at least 10 nanometres to less than 1 μm; and the dispersion has a solids content of greater than 15 wt %.

2. The method of claim 1, wherein the dispersion has total base number ranging from 200 to 1750.

3. The method of claim 1, wherein the dispersion is semi-translucent to translucent or transparent.

4. The method of claim 1, wherein the physical processes for preparing the dispersion comprise milling in a vertical or horizontal bead mill.

5. The method of claim 1, wherein the metal base is present at 25 wt % to 80 wt %, or from 35 wt % to 70 wt % of the dispersion.

6. The method of claim 1, wherein the metal of the metal base comprises a monovalent or divalent metal.

7. The method of claim 1, wherein the metal comprises lithium, potassium, sodium, copper, zinc, magnesium, calcium, barium or mixtures thereof.

8. The method of claim 1, wherein the metal comprises calcium.

9. The method of claim 1, wherein the metal base has a mean average particle size of 30 nanometres to 0.7 μm.

10. The method of claim 1, wherein the base of the metal base comprises at least one of oxides, hydroxides or carbonates.

11. The method of claim 1, wherein the metal base comprises sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, sodium hydroxide, potassium hydroxide, anhydrous lithium hydroxide, lithium hydroxide monohydrate, magnesium hydroxide, calcium hydroxide, lithium carbonate, calcium carbonate, copper acetate, magnesium carbonate, calcium

oxide, magnesium oxide, lithium oxide, cerium oxide, iron oxide or mixtures thereof.

12. The method of claim 1, wherein the surfactant has a hydrophilic lipophilic balance (HLB) ranging from 1 to 40.

13. The method of claim 1, wherein the surfactant comprises at least one of hydrocarbyl substituted aryl sulphonic acids, polyolefin-substituted acylating agents, or salixarenes.

14. The method of claim 1, wherein the organic medium comprises an oil of lubricating viscosity.

15. The method of claim 1, wherein the dispersion comprises: (a) 40-65 wt % of a metal base; (b) 5-25 wt % of a surfactant; and (c) an organic medium in which the metal base is uniformly dispersed by physical processes.

16. A lubricant composition comprising (i) a dispersion comprising: (a) a metal base; (b) a surfactant; and (c) an organic medium in which the metal base is uniformly dispersed by physical processes, wherein the metal base has a mean average particle size of at least 10 nanometres to less than 1 μm; and the dispersion has a solids content of greater than 15 wt %; (ii) an oil of lubricating viscosity; and (iii) other performance additives.

17. The lubricant composition of claim 16, wherein the other performance additives comprise at least one of metal deactivators, detergents, dispersants, viscosity modifiers, friction modifiers, corrosion inhibitors, dispersant viscosity modifiers, extreme pressure agents, antiscuffing agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof.

18. The lubricant composition of claim 16, wherein (i) the dispersion is present at 0.5-10 wt % (ii) the oil of lubricating viscosity is present at 70-99.4 wt %; and (iii) the other performance additives are present at 0.01-25 wt % of the lubricant composition.