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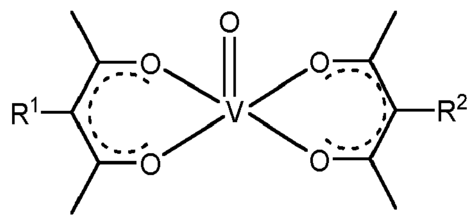
(54) LUBRICATING OIL COMPOSITIONS

(57) A lubricating oil composition comprises at least 50 percent by mass, based on the mass of the composition of an oil of lubricating viscosity and 0.01 to 25 percent by mass, based on the mass of the composition, of a compound having structure (I):



(I)

wherein R^1 and R^2 are the same or different and are linear or branched alkyl groups having from 2 to 10, preferably from 2 to 8 carbon atoms. The compositions provide wear protection between sliding metal contacts, such as may be found in engines.

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Description

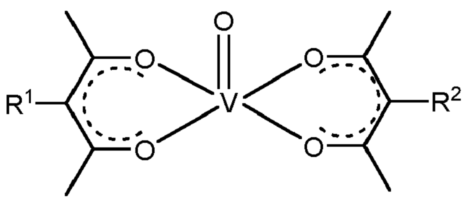
[0001] This invention relates to lubricating oil compositions containing certain vanadium compounds. The compounds provide the compositions with friction reducing and anti-wear properties. The lubricating oil compositions are useful in the lubrication of internal combustion engines, such as those found in vehicles.

[0002] Metal-containing additives have long been used in lubricating oil compositions of various types. For example, zinc dialkyldithiophosphate (ZDDP) compounds are known to be multi-functional, providing wear protection to surfaces lubricated by the oil compositions as well as improving the oxidation resistance of the oil. Molybdenum-containing compounds of different kinds are also used to improve the oxidation resistance of oils as well as providing friction modification properties. Detergent compounds based on alkali and alkaline-earth metals are also widely used. However, compounds of vanadium have historically been less commonly used.

[0003] US 2,795,549 describes certain metal complexes containing *inter alia,* acids, oxides or salts of vanadium, tungsten or zirconium together with a chelating compound having two functional groups vicinal to one another. Particular examples of chelating compounds include acetylacetone and vanadium is a preferred metal. The compounds, for example, vanadyl bisacetylacetonate, are indicated to limit the oxidation of lubricating oils and to provide some protection to copper and lead-containing materials from corrosion.

[0004] It has now been found that certain specific complexes of vanadium, with particular chelating groups distinct from those described in US 2,795,549, are able to provide excellent wear protection and friction reduction properties to lubricating oil compositions. These advantageous effects are not seen for the compounds described in US 2,795,549.

[0005] Accordingly, in a first aspect, the present invention provides a lubricating oil composition comprising at least 50 percent by mass, based on the mass of the composition of an oil of lubricating viscosity and 0.01 to 15 percent by mass, based on the mass of the composition, of a compound having structure (I):



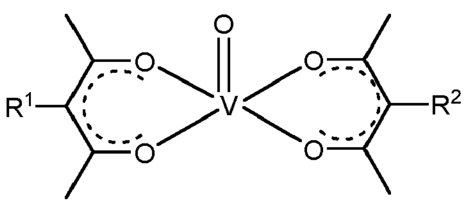
(I)

wherein R^1 and R^2 are the same or different and are linear or branched alkyl groups having from 2 to 10, preferably from 2 to 8 carbon atoms.

[0006] The lubricating oil composition may comprise a single compound of structure (I) or two or more different compounds of structures (I) and (II).

[0007] In a second aspect, the present invention provides a method of reducing friction and/or wear between contacting surfaces of a machine, the method comprising supplying a lubricating oil composition according to the first aspect to the contacting surfaces.

[0008] In a third aspect, the present invention provides the use of a compound having structure (I):



(I)

wherein R^1 and R^2 are the same or different and are linear or branched alkyl groups having from 2 to 10, preferably from 2 to 8 carbon atoms as an additive in a lubricating oil composition to reduce friction and/or wear between contacting surfaces of a machine lubricated by the composition,

wherein the composition comprises least 50 percent by mass, based on the mass of the composition of an oil of lubricating viscosity and 0.01 to 15 percent by mass, based on the mass of the composition of the compound of structure (I).

[0009] Preferably in all aspects, the compound having structure (I) is present in the lubricating oil composition in an amount of 0.01 to 10 percent by mass, based on the mass of the composition, more preferably 0.05 to 5 percent by mass, even more preferably 0.1 to 1 percent by mass.

[0010] The amount of compound of structure (I) present may alternatively be expressed in terms of the mass of vanadium present in the lubricating oil composition so preferably, in all aspects, the compound of structure (I) is present in an amount such as to provide the lubricating oil composition with 10 to 10,000 parts per million by mass (ppm) of vanadium, more preferably 50 to 5,000 ppm, even more preferably 50 to 1,500 ppm.

[0011] In a preferred embodiment of the second and third aspect of the invention, the machine having contacting surfaces lubricated by the composition is an internal combustion engine. Suitable engines will be known to those skilled in the art and include both spark-ignited (gasoline) and compression-ignited (diesel) engines such as may be found in automotive engines used in cars, trucks, buses and other land vehicles, as well as engines used in marine applications. The contacting surfaces of the engine lubricated by the composition may be those found for example, in the crank-case of the engine. The lubricating oil compositions of the present invention may also find use in the lubrication of gears and manual or automatic transmission systems.

[0012] In the description that follows, all elements described are applicable to all aspects of the invention.

DETAILED DESCRIPTION OF THE INVENTION

DEFINITIONS

[0013] In this specification, the following words and expressions, if and when used, have the meaning given below:

"active ingredients" or "(a.i.)" refers to additive material that is not diluent or solvent;

"comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions "consists of' or "consists essentially of' or cognates may be embraced within "comprises" or any cognate word. The expression "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies. The expression "consists of" or cognates means only the stated features, steps, integers components or groups thereof are present to which the expression refers;

"hydrocarbyl" means a chemical group of a compound that contains hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom. The use of the qualifier "substituted" means that the hydrocarbyl group may contain one or more atoms other than carbon and hydrogen ("hetero atoms"). Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, carboxy, ester, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.). The group may be unsaturated, and/or may be polymeric;

"oil-soluble" or "oil-dispersible", or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired;

"ashless" in relation to an additive means the additive does not include a metal;

"ash-containing" in relation to an additive means the additive includes a metal;

"major amount" means in excess of 50 mass % of a composition or mixture;

"minor amount" means 50 mass % or less of a composition or mixture;

"effective amount" in respect of an additive means an amount of such an additive in the composition (e.g. an additive concentrate) that is effective to provide, and provides, the desired technical effect;

"ppm" means parts per million by mass, based on the total mass of the composition;

"metal content" of a composition or of an additive component, for example molybdenum content or total metal content of the additive concentrate (i.e. the sum of all individual metal contents), is measured by ASTM D5185;

"TBN" in relation to an additive component or of a composition, means total base number (mg KOH/g) as measured by ASTM D2896;

"KVioo" means kinematic viscosity at 100°C as measured by ASTM D445;

HTHS means High Temperature High Shear at 150°C as measured by CEC-L-36-A-90.

"phosphorus content" is measured by ASTM D5185;

"sulphur content" is measured by ASTM D2622;

"sulfated ash content" is measured by ASTM D874;

M_n means number average molecular weight as measured by Gel Permeation Chromatography with reference to linear narrow poly(methylmethacrylate) standards in the range of 550 to 600,000 g/mol;

M_w means weight average molecular weight as measured by Gel Permeation Chromatography with reference to linear narrow poly(methylmethacrylate) standards in the range of 550 to 600,000 g/mol;

"dispersity" means M_w/M_n, (denoted by Đ)

[0014] Also, it will be understood that various components used, essential as well as optimal and customary, may react under condition of formulation, storage and use and that the invention also provides the product(s) obtainable or obtained by any such reaction.

[0015] Further it is understood that any upper and lower quality, range or ratio limits set forth herein may be independently combined.

Compounds of structure (I)

[0016] Compounds of structure (I) have a vanadyl core (VO^{2+}) co-ordinated to a ligand system comprised of two bidentate ligands. The ligands are acetylacetonate ligands where the central carbon atom carries a linear or branched alkyl group.

[0017] Those skilled in the art will appreciate that structure (I) is a simplified representation of the compounds indicating that there will exist resonance forms where formal single and double bonds are interchangeable.

[0018] Furthermore, structure (I) is shown without any stereochemical indications for reasons of clarity. Those skilled in the art will understand that the compounds are not planar. The ligands around the vanadyl centre will normally be arranged in a square pyramid form.

[0019] Preferred linear alkyl groups suitable as R^1 and R^2 include ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl.

[0020] Preferred branched chain alkyl groups suitable as R^1 and R^2 include isopropyl, methylpropyl, secondary-butyl, tertiary-butyl, methylbutyl, dimethylpropyl, methylpentyl, dimethylbutyl, ethylbutyl, methylhexyl, dimethylpentyl, ethylpentyl, and 2-ethylhexyl.

[0021] In a preferred embodiment, R^1 and R^2 are the same or different and are linear alkyl groups.

[0022] In particularly preferred embodiments, at least one of R^1 and R^2 is n-propyl, n-butyl, n-hexyl or n-octyl.

[0023] In a particularly preferred embodiment, R^1 and R^2 are the same.

[0024] Those skilled in the art will be aware of a number of different synthetic routes to the compounds used in the present invention. One non-limiting example of a general synthetic approach is given in the following section. Alterations to solvent and other synthetic steps can be made to optimise the reaction dependent on reagent choice.

[0025] Vanadyl (IV) sulfate hydrate (1 eq.) and sodium acetate (2.05 eq.) were combined in a suitably sized round bottom flask prior to flushing with dry N_2. After the addition of ethanol, the pale blue suspension obtained was degassed via N_2 sparging and an alkylpentane-2,4-dione ligand (2.05 eq.) was added slowly via syringe, resulting in a green/blue solution. Water was added until a dark green solution was afforded, with all solids dissolved. On partition of a dark green oil, more water was added to promote further precipitation. Stirring in an ice/water bath ensured full precipitation and solidification of the green oil. The solid was isolated via vacuum filtration on a glass frit, thoroughly washed with water and ethanol to remove residual starting materials and impurities. After final washing with heptane the resultant green solid was dried under vacuum.

LUBRICATING OIL COMPOSITIONS

[0026] Lubricating oil compositions of the invention may be lubricants suitable for use as motor vehicle motor oils comprising a major amount of oil of lubricating viscosity and minor amounts of performance-enhancing additives, including the compounds of the present invention. The lubricating oil composition may also be in the form of an additive concentrate for blending with oil of lubricating viscosity to make a final lubricant.

[0027] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making additive concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural oils (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[0028] Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998, which categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.

d) Group IV base stocks are polyalphaolefins (PAO).

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[0029] Typically, the base stock has a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8, mm^2/s at 100°C.

Table E-1: Analytical Methods for Base Stock

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

[0030] Preferably, the oil of lubricating viscosity comprises greater than or equal to 10, more preferably greater than or equal to 20, even more preferably greater than or equal to 25, even more preferably greater than or equal to 30, even more preferably greater than or equal to 40, even more preferably greater than or equal to 45, mass % of a Group II or Group III base stock, based on the total mass of the oil of lubricating viscosity. Even more preferably, the oil of lubricating viscosity comprises greater than 50, preferably greater than or equal to 60, more preferably greater than or equal to 70, even more preferably greater than or equal to 80, even more preferably greater than or equal to 90, mass % of a Group II or Group III base stock, based on the total mass of the oil of lubricating viscosity. Most preferably, the oil of lubricating viscosity consists essentially of a Group II and/or Group III base stock. In some embodiments the oil of lubricating viscosity consists solely of Group II and/or Group III base stock. In the latter case it is acknowledged that additives included in the lubricating oil composition may comprise a carrier oil which is not a Group II or Group III base stock.

[0031] Other oils of lubricating viscosity that may be included in the lubricating oil composition are detailed as follows: Natural oils include animal and vegetable oils (e.g. castor and lard oil), liquid petroleum oils and hydro refined, solvent-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.

[0032] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

[0033] Another suitable class of synthetic lubricating oil 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, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g. 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, dieicosyl 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.

[0034] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0035] Unrefined, refined and re-refined oils can be used in the 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 unrefined oil. 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. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation, are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils that have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for treating spent additive and oil breakdown products.

[0036] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

[0037] The oil of lubricating viscosity may also comprise a Group I, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks.

[0038] The lubricating compositions of the present invention preferably comprise at least 60% by weight, for example 70% by weight or more of an oil of lubricating viscosity, based on the weight of the composition.

CO-ADDITIVES

[0039] The lubricating oil compositions of the present invention may further comprise additives other than a compound of formula (I). These are discussed in more detail below.

[0040] A dispersant is an additive whose primary function is to hold solid and liquid contaminants in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine. Dispersants have been used in lubricating oil compositions widely and for many years. Their structures and chemistries are well known to those skilled in the art.

[0041] Dispersants are preferably "ashless", being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of e.g. an O, P, or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

[0042] A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream.

[0043] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine.

Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; -3,154,560; -3,172,892; -3,024,195; -3,024,237, -3,219,666; and -3,216,936, that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and -3,254,025), fluorinated or oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

[0044] Preferred dispersants are succinimide-dispersants derived from a polyisobutene of number average molecular weight in the range of 1000 to 3000, preferably 1500 to 2500, and of moderate functionality. The succinimide is preferably derived from highly reactive polyisobutene.

[0045] Where a dispersant is present, preferably the dispersant comprises from 0.1 to 20 mass% of the lubricating oil composition, based on the mass of the composition, more preferably, from 0.1 to 10 mass%.

[0046] Oxidation inhibitors or antioxidants reduce the tendency of oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, 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 C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons or esters, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds.

[0047] Aromatic amines having at least two aromatic groups attached directly to the nitrogen constitute another class of compounds that is frequently used for antioxidancy. Typical oil-soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, $-SO_2-$ or alkylene group) and two are directly attached to one amine nitrogen are also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups. The amount of any such oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen should preferably not exceed 0.4 mass %.

[0048] A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits in engines; it normally has acid-neutralising properties and is capable of keeping finely-divided solids in suspension. Most detergents are based on metal "soaps", that is metal salts of acidic organic compounds.

[0049] Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising the metal salt of the acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN at 100 % active mass (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reaction of an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide.

[0050] The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN at 100 % active mass of 150 or greater, and typically of from 200 to 500 or more.

[0051] Suitably, detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurised phenates, thiophosphonates, salicylates and naphthenates and other oil-soluble carboxylates of a metal, particularly alkali metal or alkaline earth metals, e.g. Na, K, Li, Ca and Mg. The most commonly-used metals are Ca and Mg, which may both be present in detergents used in lubricating compositions, and mixtures of Ca and/or Mg with Na. Detergents may be used in various combinations.

[0052] Friction modifiers and fuel economy agents may also be included. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; and alkoxylated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

[0053] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil-soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0054] Additionally, the molybdenum compound may be an acidic molybdenum compound. 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 alkali metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, $MoOCl_4$, MoO_2Br_2, $Mo_2O_3Cl_6$, molybdenum trioxide or similar acidic molybdenum compounds.

[0055] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formula

$Mo(R''OCS_2)_4$

and

$Mo(R''SCS_2)_4$

wherein R" is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0056] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear molybdenum compounds, especially those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein the L are 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 to 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. At least 21 carbon atoms should be present among all the ligand organo groups, such as at least 25, at least 30, or at least 35, carbon atoms.

[0057] Lubricating oil compositions useful in all aspects of the present invention preferably contain at least 10 ppm, at least 30 ppm, at least 40 ppm and more preferably at least 50 ppm molybdenum. Suitably, lubricating oil compositions useful in all aspects of the present invention contain no more than 1000 ppm, no more than 750 ppm or no more than 500 ppm of molybdenum. Lubricating oil compositions useful in all aspects of the present invention preferably contain from 10 to 1000, such as 30 to 750 or 40 to 500, ppm of molybdenum (measured as atoms of molybdenum).

[0058] The viscosity index of the oil of lubricating viscosity may be increased, or improved, by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (Mn) of from 5,000 to 250,000, preferably from 15,000 to 200,000, more preferably from 20,000 to 150,000. These viscosity modifiers can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional viscosity modifiers (dispersant-viscosity modifiers).

[0059] Polymers prepared with diolefins will contain ethylenic unsaturation, and such polymers are preferably hydrogenated. When the polymer is hydrogenated, the hydrogenation may be accomplished using any of the techniques known in the prior art. For example, the hydrogenation may be accomplished such that both ethylenic and aromatic unsaturation is converted (saturated) using methods such as those taught, for example, in U.S. Pat. Nos. 3,113,986 and 3,700,633 or the hydrogenation may be accomplished selectively such that a significant portion of the ethylenic unsaturation is converted while little or no aromatic unsaturation is converted as taught, for example, in U.S. Pat. Nos. 3,634,595; 3,670,054; 3,700,633 and Re 27,145. Any of these methods can also be used to hydrogenate polymers containing only ethylenic unsaturation and which are free of aromatic unsaturation.

[0060] Pour point depressants (PPD), otherwise known as lube oil flow improvers (LOFIs) lower the lowest temperature at which the lube flows. Compared to VM, LOFIs generally have a lower number average molecular weight. Like VM, LOFIs can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional additives.

[0061] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount that enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below. All the values listed (with the exception of detergent values since the detergents are used in the form of colloidal dispersants in an oil) are stated as mass percent active ingredient (A.I.).

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Dispersants	0.1 - 20	0.1 - 10
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitor	0 - 5	0 - 1.5
Antioxidant	0 - 5	0.01 - 2.5
Pour Point Depressant	0.01 - 5	0.01 - 1.5

(continued)

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Antifoaming Agent	0 - 5	0.001 - 0.15
Supplemental Antiwear Agents	0 - 1.0	0 - 0.5
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 10	0.25 - 3
Base stock	Balance	Balance

[0062] Preferably, the Noack volatility of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives) is no greater than 18, such as no greater than 14, preferably no greater than 10, mass %. Lubricating oil compositions useful in the practice of the present invention may have an overall sulfated ash content of from 0.5 to 2.0, such as from 0.7 to 1.4, preferably from 0.6 to 1.2, mass %.

[0063] It may be desirable, although not essential, to prepare one or more additive concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition.

EXAMPLES

[0064] The four compounds listed in the table below were obtained/synthesised as follows:

Compound A

[0065] Purchased from Sigma Aldrich (CAS: 3153-26-2).

Compound 1 — R^1, R^2 = n-propyl

[0066] Vanadyl (IV) sulfate hydrate (6.33 g, 25 mmol) and sodium acetate (4.10 g, 50 mmol) were combined in a 250 mL round bottom flask which was subsequently flushed with dry N_2. After the addition of ethanol (40 mL), the pale blue suspension obtained was degassed via N_2 sparging, and 3-propylpentane-2,4-dione (7.11 g, 50 mmol) was added slowly via syringe resulting in a green/blue solution. 20 mL of water was added until a dark green solution was afforded, with all solids dissolved. After 5 minutes and the partition of a dark green oil, a further 20 mL of water was added. Stirring in an ice/water bath for 2 hours ensured full precipitation and solidification of the green oil, after which the solid was isolated via vacuum filtration on a glass frit. The solid was washed with water (5 × 10 mL) and ethanol (1 × 10 mL) to remove residual starting materials and impurities, after which 2 × 20 mL hexane washes were carried out before drying under vacuum for 2 hours at 25 °C. (Yield 5.01 g, 57 %)

Compound 2 — R^1, R^2 = n-butyl

[0067] Vanadyl (IV) sulfate hydrate (5 g, 21.3 mmol) and sodium acetate (3.58 g, 43.6 mmol) were combined in a 100 mL round bottom flask which was subsequently flushed with dry N_2. After the addition of 2-propanol (25 mL), the pale blue suspension was degassed via N_2 sparging and 3-propylpentane-2,4-dione (6.81 g, 43.6 mmol) was added slowly via syringe. 50 mL of water was added until a dark green solution was afforded, with all solids dissolved. During addition, dark green solid precipitated and the resultant suspension was stirred for 10 minutes, cooled to 2 °C in an ice/water bath for 15 minutes, and the solid isolated via vacuum filtration on a glass frit. The filter cake was washed with water until the filtrate ran clear, before drying in a vacuum oven overnight at 60 °C. (Yield 4.60 g, 57 %)

Compound 3 — R^1, R^2 = n-octyl

[0068] Vanadyl (IV) sulfate hydrate (2.00 g, 8.51 mmol) and sodium acetate (1.43 g, 17.44 mmol) were combined in a 100 mL round bottom flask which was subsequently flushed with dry N_2. After the addition of ethanol (40 mL), the pale blue suspension was degassed via N_2 sparging, and 3-octylpentane-2,4-dione (3.70 g, 17.44 mmol) was added slowly via syringe resulting in a green/blue solution. 20 mL of water was added until a dark green solution was afforded, with all solids dissolved. After 5 minutes and the partition of a dark green oil a further 20 mL of water was added. Stirring in an ice/water bath for 2 hours ensured full precipitation and solidification of the green oil, after which the solid was isolated via vacuum filtration on a glass frit. 3 × 10 mL washes with water and ethanol respectively removed residual starting materials and impurities, after which 3 × 5 mL heptane washes were carried out prior to vacuum drying for 2 hours at 40 °C. (Yield 2.73 g, 66 %).

Compound	Group R^1	Group R^2
A	none	none
1	n-propyl	n-propyl
2	n-butyl	n-butyl
3	n-octyl	n-octyl

[0069] Oil compositions were then formed by adding each of the compounds to a Group III mineral oil (Yubase 4) in an amount such as to provide the oil compositions with 250 parts per million by mass of vanadium. Oil A contained Compound A, Oil 1 contained Compound 1, Oil 2 contained Compound 2, and Oil 3 contained Compound 3.

[0070] Compound A is vanadyl bisacetylacetonate so is the compound described in US 2,795,549. Oil A is thus used here as a comparative example. Oils 1, 2 and 3 are examples of the present invention as they contain Compounds 1, 2 and 3 which all conform to Structure (I).

[0071] The oils were tested using a High Frequency Reciprocating Rig (HFRR) available from PCS Instruments, London. In this test, a steel ball is loaded and reciprocated against the face of a steel disc. The load between the ball and the disc was set at 4N giving a contact pressure of 1.046 Gpa. The ball was driven with a frequency of 40Hz over a stroke length of 1mm for a duration of 1 hour and at oil temperatures increasing from 40°C to 140°C.

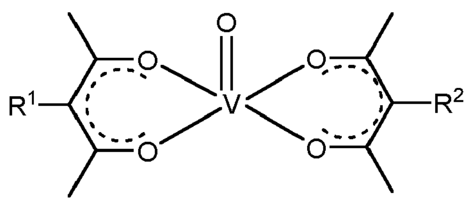
[0072] Each oil was tested in the same way a further two times and the average wear scar volume was calculated. Results are shown in the table below.

Oil	HFRR wear scar volume / μm^3
A	356449
1	168853
2	170390
3	221010

[0073] It can clearly be seen that the compared to Oil A, the compositions according to the present invention provided significantly better wear protection, as evidenced by the lower wear scar volumes measured.

Claims

1. A lubricating oil composition comprising at least 50 percent by mass, based on the mass of the composition of an oil of lubricating viscosity and 0.01 to 25 percent by mass, based on the mass of the composition, of a compound having structure (I):



(I)

wherein R^1 and R^2 are the same or different and are linear or branched alkyl groups having from 2 to 10, preferably from 2 to 8 carbon atoms.

2. A lubricating oil composition according to claim 1 wherein R^1 and R^2 are the same or different and are linear alkyl groups.

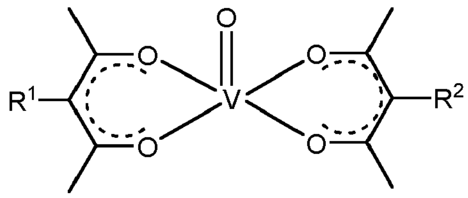
3. A lubricating oil composition according to claim 1 or claim 2 wherein at least one of R^1 and R^2 is n-propyl, n-butyl, n-hexyl or n-octyl.

4. A lubricating oil composition according to any preceding claim wherein R^1 and R^2 are the same.

5. A lubricating oil composition according to any preceding claim comprising one or more co-additives different from the compound having structure (I), the one or more co-additives being selected from dispersants, oxidation inhibitors or anti-oxidants, detergents, friction modifiers, and viscosity modifiers.

6. A method of reducing friction and/or wear between contacting surfaces of a machine, the method comprising supplying a lubricating oil composition according to any preceding claims to the contacting surfaces.

7. The use of a compound having structure (I):



(I)

wherein R^1 and R^2 are the same or different and are linear or branched alkyl groups having from 2 to 10, preferably from 2 to 8 carbon atoms as an additive in a lubricating oil composition to reduce friction and/or wear between contacting surfaces of a machine lubricated by the composition,
wherein the composition comprises least 50 percent by mass, based on the mass of the composition of an oil of lubricating viscosity and 0.01 to 25 percent by mass, based on the mass of the composition of the compound of structure (I).

8. The method of claim 6 or the use of claim 7 wherein the machine having contacting surfaces lubricated by the composition is an internal combustion engine.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 20 0776

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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1 The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	1 March 2022	Klaes, Daphne

CATEGORY OF CITED DOCUMENTS

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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