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(54) Lubricating Compositions

(57) A lubricating oil composition, comprising as an ester additive component, one or more esters of glycerol and a carboxylic acid such as oleic acid having a defined proportion of monoester, diester and/or triester and an oil-soluble molybdenum compound, which may a trinuclear molybdenum compound.

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Description

[0001] This invention relates to compositions such as lubricating oil compositions, more especially to compositions suitable for use in piston engines, especially gasoline (spark-ignited) and diesel (compression-ignited), crankcase lubrication, such compositions being referred to as crankcase lubricants; to additive concentrates therefor; and to use of additives in friction modification.

[0002] A crankcase lubricating oil composition, or lubricant, is an oil used for general lubrication in an engine where there is an oil sump below the crankshaft of the engine and to which circulated oil returns. It is well-known to include additives in crankcase lubricants for several purposes.

[0003] The invention concerns use of organic friction modifiers in crankcase lubrication. Friction modifiers, also referred to as friction-reducing agents, may be boundary additives that operate by lowering friction coefficient and hence improve fuel economy.

[0004] The use of glycerol monoesters as friction modifiers has been described in the art, for example in US-A-4,495,088; US-A-4,683,069; EP-A-0 092 946; and WO-A-01/72933. One or more of these documents indicate that what is often referred to as glycerol mono-oleate, in its commercially available form, is a mixture that includes the diester and that, when glycerol is esterified with a fatty acid, mono-, di- and triesters form. Also, certain of the above listed documents teach that the proportion of monoester in the mixture is high and EP-A-0 092 946 teaches the use of essentially all monoester in an ester component.

[0005] WO-A-01/72933 (referred to above) and US-B-6,723,685 each describe the use of a glycerol ester additive in combination with a molybdenum compound in lubricating oil compositions. But WO-A-01/72933 requires the monoester content of the ester additive to be at least 75 mole percent and, in a comparative example, refers to use of 68 mole percent of monoester in combination with a molybdenum compound and US-B-6,723,685 makes no reference to the monoester content.

[0006] EP-A-0 743 354 discloses a lubricating oil providing improved wear protection comprising an alkylamine phosphate and at least one additive selected from the group comprising oxymolybdenum sulphide dithiocarbamate, oxymolybdenum sulphide organophosphorosithioate, fatty ester and organic amides. The examples of EP-A-0 743 354 include use of a fatty ester comprising 50% monoester. WO-A-96/37581 discloses a lubricating oil composition comprising a metal dithiocarbamate extreme pressure agent of specific formula, wherein the metal may be molybdenum or tungsten, which is said to exhibit excellent wear resistance, extreme-pressure lubricity and low coefficient of friction. The lubricating oil composition may additionally comprise a fatty acid ester, and example 2 uses a fatty acid ester comprising 50% monoester.

[0007] A problem faced by formulators of lubricants is to reduce the amount of fuel consumed in operation of piston engines. The present invention provides, surprisingly, as evidenced by the data in this specification, an improvement in friction modification at higher temperatures by employing, in combination with molybdenum compounds, glycerol ester additives in which the proportions of monoester thereof is controlled.

[0008] Thus, in a first aspect, this invention provides a composition comprising:

(A) an oil of lubricating viscosity;

(B) as an ester additive component, one or more esters of glycerol and a carboxylic acid containing 12 to 30 carbon atoms and 0 to 3 carbon-carbon double bonds wherein less than 50% by mass of the component is one or more monoesters; and

(C) as a further additive component, an oil-soluble molybdenum compound.

[0009] In a second aspect, this invention provides a method for improving the friction modification of an internal combustion engine at high temperature comprising operating the engine and lubricating the engine with a composition according to the first aspect of the invention.

[0010] In a third aspect, this invention provides the use of an additive (B) in combination with an additive (C), as defined in the first aspect of the invention, for enhancing the high-temperature friction-modification properties of a lubricating oil composition in the lubrication of an internal combustion engine.

[0011] In a fourth aspect, this invention provides a composition comprising:

(A) an oil of lubricating viscosity;

(B) as an ester additive component, one or more esters of glycerol and a carboxylic acid containing 12 to 30 carbon atoms and 0 to 3 carbon-carbon double bonds wherein less than 55% by mass of the component is one or more monoesters; and

(C) as a further additive component, an oil-soluble tri-nuclear molybdenum compound.

[0012] In a fifth aspect, this invention provides a method for improving the friction modification of an internal combustion engine at high temperature comprising operating the engine and lubricating the engine with a composition according to the fourth aspect of the invention.

[0013] In a sixth aspect, this invention provides the use of an additive (B) in combination with an additive (C), as defined in the fourth aspect of the invention, for enhancing the high-temperature friction-modification properties of a lubricating oil composition in the lubrication of an internal combustion engine.

[0014] In this specification, the following words and expressions shall have the meanings ascribed 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 cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

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

"minor amount" means less than 50 mass % of a composition.

[0015] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0016] Further, it is to be understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0017] The features of the invention relating, unless otherwise specified, to each and all aspects of the invention, will now be described in more detail as follows:

Additive Component (B)

[0018] The carboxylic acid is preferably a saturated or unsaturated C16 to C18 fatty acid, such as oleic acid.

[0019] Preferably, in respect of the first aspect of the invention the component contains, as lower limits, 1, 5 or 10, and, as upper limits, 30, 40 or 45, mass % of one or more monoesters, which upper and lower limits may be independently combined. Preferably, in respect of the fourth aspect of the invention the component contains, as lower limits, 1, 5 or 10, and, as upper limits, 30, 40, 45 or 50, mass % of one or more monoesters, which upper and lower limits may be independently combined.

[0020] In one embodiment of either the first aspect of the invention or the fourth aspect of the invention, the component consists of partial esters only, ie of mono- and diesters; this embodiment contains less than 40, such as 5 to less than 40, % by mass of one or more monoesters, ie 60 or more, such as 60 to 95, % by mass of one or more diesters.

[0021] In either the first or the fourth embodiment, where one or more triesters are present in the component, they may constitute 60 or more, such as 60 to 95, % by mass of the component.

[0022] In another embodiment, monoesters may be absent from the component, when the component consists wholly of diester(s) or wholly of triester(s) or wholly of mixtures thereof.

[0023] The esters may be borated, for example as described in above-mentioned WO-A-01/72933.

Oil of Lubricating Viscosity (A)

[0024] 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).

[0025] A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil and heavy duty diesel oil. Generally the viscosity of the oil ranges from 2 to 30, especially 5 to 20, mm^2s^{-1} at 100°C.

[0026] Natural oils include animal and vegetable oils (e.g. castor and lard oil) liquid petroleum oils and hydrorefined, 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.

[0027] 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; analogs and homologs thereof.

[0028] Another suitable class of synthetic lubricating oils 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.

[0029] 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.

[0030] Unrefined, refined and re-refined oils can be used in the lubricants 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 which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additional processed by techniques for approval of spent additive and oil breakdown products.

[0031] Other examples of base oil are gas-to-liquid ("GTL") base oils, ie 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.

[0032] Base oil may be categorised in Groups I to V according to the API EOLCS 1509 definition.

[0033] The oil may be present in a concentrate-forming amount (e.g., from 30 to 70, such as 40 to 60, mass %) so that the composition is in the form of a concentrate containing for example 1 to 90, such as 10 to 80, preferably 20 to 80, more preferably 20 to 70, mass % active ingredient of an additive or additives, being components (B) and (C) above, or a combination of components (B) and (C) and one or more co-additives.

[0034] The oil of lubricating viscosity used in a concentrate is a suitable oleaginous, typically hydrocarbon, carrier fluid, e.g. mineral lubricating oil, or other suitable solvent. Oils of lubricating viscosity such as described herein, as well as aliphatic, naphthenic, and aromatic hydrocarbons are examples of suitable carrier fluids for concentrates.

[0035] Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additive in lubricating oil compositions. When preparing a lubricating oil composition that contains more than one type of additive (sometime referred to as "additive components"), each additive may be incorporated separately - each in the form of a concentrate. In many instances, however, it is convenient to provide a so-called additive "package" (also referred to as an "adpack") comprising two or more additives in a single concentrate.

[0036] The oil of lubricating viscosity may be provided in a major amount, in combination with a minor amount of component (B) and component (C) and, if necessary, a minor amount of one or more co-additives such as described hereinafter, constituting a lubricating oil composition. This preparation may be accomplished by adding the additive directly to the oil or by adding it in the form of a concentrate thereof to disperse or dissolve the additive. Additives may be added to the oil by any method known to those skilled in the art, either prior to, contemporaneously with, or subsequent to addition of other additives.

Additive Component (C)

[0037] In respect of the first aspect of the invention, any suitable oil-soluble organo-molybdenum compound having friction modifying and/or anti-wear properties in lubricating oil compositions may be employed. As an example of such oil-soluble organo-molybdenum compounds, there may be mentioned the dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0038] The molybdenum compound may be mono, di-, tri- or tetra-nuclear. Dinuclear and trinuclear molybdenum compounds are preferred.

[0039] 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 alkaline metal molybdates and other molybdenum salts, eg, hydrogen sodium molybdates, $MoOCl_4$, MoO_2Br_2 $Mo_2O_3Cl_6$, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions of the present invention can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as describes, for example, in US Patent Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and WO 94/06897.

[0040] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formulae.

$Mo(ROCS_2)_4$ and

$M_O(RSCS_2)_4$

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.

[0041] In respect of the fourth aspect of the invention, any suitable tri-nuclear oil-soluble organo-molybdenum compound having friction modifying and/or anti-wear properties in lubricating oil compositions may be employed. As an example of such oil-soluble organo-molybdenum compounds, there may be mentioned the dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

The tri-nuclear molybdenum compound of the fourth aspect of the invention may comprise tetra-nuclear molybdenum compound. Preferably, the tri-nuclear molybdenum compound comprises at least 90%, preferably at least 95% and more preferably substantially 100% tri-nuclear molybdenum compound.

[0042] One class of preferred organo-molybdenum compounds useful in all aspects of the present invention are tri-nuclear molybdenum compounds of the formula $Mo_3S_kL_nQ_Z$ and mixtures thereof wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compounds soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 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 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0043] The terms "oil-soluble" or "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 instance, 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.

[0044] The lubricating oil compositions may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited, compression-ignited two or four stroke reciprocating engines, by adding the composition thereto.

[0045] The lubricating oil compositions and concentrates comprise defined components that may or may not remain the same chemically before and after mixing with an oleaginous carrier. This invention encompasses compositions and concentrates which comprise the defined components before mixing, or after mixing, or both before and after mixing.

[0046] When concentrates are used to make the lubricating oil compositions, they may for example be diluted with 3 to 100, e.g. 5 to 40, parts by weight of oil of lubricating viscosity per part of the concentrate.

[0047] In lubricating oil compositions of this invention, representative effective amounts of additive component (B), as an organic friction modifier, are from 0.05 to 5, such as 0.05 to 0.3 or to 0.6 or to 1.5, mass %.

[0048] The lubricating oil compositions of the present invention may contain the molybdenum compound, (C), in an amount providing the composition with at least 10, such as 50 to 2000 ppm of molybdenum. Preferably, the molybdenum from the molybdenum compound is present in an amount of from 10 ppm to 1500 ppm, such as 20 ppm to 1000 ppm, more preferably from 30 ppm to 750 ppm, based on the total weight of the lubricating oil composition. For some applications, the molybdenum is present in an amount of greater than 500 ppm.

[0049] Other co-additives, with representative effective amounts in lubricating oil compositions are listed below. All the values listed are stated as mass percent active ingredient.

ADDITIVE	**MASS %** (Broad)	**MASS %** (Preferred)
Ashless Dispersant	0.1 - 20	1 - 8
Metal Detergents	0.1 - 6	0.2-4
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 10	0.2-4
Anti-Oxidants	0-5	0.01 - 1.5
Pour Point Depressant	0.01 - 5	0.01-1.5
Anti-Foaming Agent	0-5	0.001-0.15
Supplemental Anti-Wear Agents	0 - 0.5	0 - 0.2
Viscosity Modifier (1)	0.01-6	0 - 4
Mineral or Synthetic Base Oil	Balance	Balance

(1) Viscosity modifiers are used only in multi-graded oils.

[0050] The final lubricating oil composition, typically made by blending the or each additive into the base oil, may contain from 5 to 25, preferably 5 to 18, typically 7 to 15, mass % of the concentrate, the remainder being oil of lubricating viscosity.

Co-Additives

[0051] The above mentioned co-additives are discussed in further detail as follows; as is known in the art, some additives can provide a multiplicity of effects - for example, a single additive may act as a dispersant and as an oxidation inhibitor.

[0052] A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. Thus, 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.

[0053] Dispersants are usually "ashless", as mentioned above, 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 chain of hydrocarbon 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.

[0054] A preferred class of olefin polymers is polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream.

[0055] 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 are hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageous 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; and BE-A-66,875 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 and 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.

[0056] 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.

[0057] Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. 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 of 150 or greater, and typically of from 250 to 500 or more.

[0058] Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g. sodium, potassium, lithium, calcium and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates and sulfurized phenates having a TBN of from 50 to 450.

[0059] Anti-oxidants are sometimes referred to as oxidation inhibitors; they increase the resistance of the composition to oxidation and may work by combining with and modifying peroxides to render them harmless, by decomposing peroxides, or by rendering an oxidation catalyst inert. Oxidative deterioration can be widened by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth.

[0060] They may be classified as radical scavengers (e.g. sterically hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e,g, organo sulphur and organophosphorus additives); and multifunctionals (e.g. zinc dihydrocarbyl dithiophosphates, which may also function as anti-wear additives, and organo-molybdenum compounds, which may also function as friction modifiers and anti-wear additives).

[0061] Examples of suitable antioxidants are selected from copper-containing antioxidants, sulphur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, metal thiocarbamates, and molybdenum-containing compounds.

[0062] Dihydrocarbyl dithiophosphate metals salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt %, based upon the total weight of the lubricating oil compositions. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 and then neutralising the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralisation reaction.

[0063] Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulphur or phosphorous or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are the dihydrocarbyl dithiophosphates, such as the zinc dialkyl dithiophosphates (ZDDP's) discussed herein as antioxidants.

[0064] Examples of ashless anti-wear agents include 1,2,3-triazoles, benzotriazoles, thiadiazoles, sulfurised fatty acid esters, and dithiocarbamate derivatives.

[0065] Rust and corrosion inhibitors serve to protect surfaces against rust and/or corrosion.

[0066] As rust inhibitors there may be mentioned non-ionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids.

[0067] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additive which improve the low temperature fluidity of the fluid are C_8 to C_{18} dialkyl fumerate/vinyl acetate copolymers and polyalkylmethacrylates.

[0068] Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane can provide foam control.

[0069] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP-A-330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

[0070] Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricating oil. Viscosity modifiers that also function as dispersants are also known and may be prepared as described above for ashless dispersants. In general, these dispersant viscosity modifiers are functionalised polymers (e.g. interpolymers of ethylene-propylene post grafted with an active monomer such as maleic anhydride) which are then derivatised with, for example, an alcohol or amine.

[0071] The lubricant may be formulated with or without a conventional viscosity modifier and with or without a dispersant viscosity modifier. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil-soluble viscosity modifying polymers generally have weight average molecular weights of from 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography or by light scattering.

EXAMPLES

[0072] The invention will now be particularly described in the following non-limiting examples.

Example 1

[0073] Four additive components were prepared consisting of various proportions of a monoester (glycerol monooleate) and a diester (glycerol dioleate). The proportions, by mass %, of the mono and diester are indicated in Table 1 below for each additive component.

Table 1

	Additive Component			
	1	2	A	B
Monoester	0	33	67	100
Diester	100	67	33	0

[0074] Components 1 and 2 were for use in examples of the invention and components A and B were for reference purposes.

[0075] Each component was blended into a lubricating oil composition, by methods known in the art, to provide a fully formulated oil composition containing 0.3 mass % of the component as active ingredient and a molybdenum additive providing 200 ppm by mass of molybdenum, and identical customary amounts of an ashless dispersant, a metal detergent, an anti-oxidant, a zinc dihydrocarbyl dithiophosphate, and an antifoam.

[0076] A high frequency reciprocating rig (HFRR) was used to evaluate the coefficient of friction characteristics of oils 1, 2, A and B. The instrument is called the AUTOHRF and is manufactured by PCS Instruments. The test protocol is shown in Table 2 below. A stepped ramp temperature profile was followed, whereby each 300 seconds the temperature was raised by a step of 20 °C and held constant for 300 seconds until the next successive 20 °C ramp.

Table 2 - HFRR Protocol

Contact	6 mm. Ball on 10 mm Disc
Load, N	3.9
Stroke Length, mm	1
Frequency, Hz.	20
Temperature range, °C	40-140
Temperature step, °C	20
Time between temperature steps, seconds	300

[0077] Results are expressed as average friction coefficient as a function of temperature and are summarised in Table 3 below, where the compositions tested are referred to as 1, 2, A and B in accordance with which additive component they contain.

Table 3 Composition

Temperature Stage (°C)	1	2	A	B
40	0.124	0.127	0.124	0.125
60	0.121	0.122	0.113	0.110
80	0.111	0.110	0.106	0.103
100	0.083	0.099	0.098	0.095
120	0.065	0.073	0.075	0.089
140	0.056	0.065	0.060	0.078

[0078] Table 3 shows that at lower temperature, Reference Examples A and B, are generally superior to Examples 1 and 2 in that they exhibit lower friction coefficients. At higher temperatures, between 80 °C and 100 °C, they become comparable. As temperature increases further, between 120 °C and 140 °C the results for Examples 1 and 2 are generally superior to those of Reference Examples A and B.

Example 2

[0079] Six additive components were prepared consisting of various proportions of a monoester (glycerol mono-oleate) and a diester (glycerol dioleate). The proportions, by mass %, of the mono and diester are indicated in Table 4 below for each additive component.

Table 4

	Additive Component					
	3	4	5	6	7	C
Monoester	0	10	20	30	45	50
Diester	100	90	80	70	55	50

[0080] Each component was blended into a lubricating oil composition, by methods known in the art, to provide a fully formulated oil composition containing 0.3 mass % of the component as active ingredient and a molybdenum additive providing 200 ppm by mass of molybdenum, and identical customary amounts of an ashless dispersant, a metal detergent, an anti-oxidant, a zinc dihydrocarbyl dithiophosphate, and an antifoam.

[0081] The high frequency reciprocating rig (HFRR) used in Example 1 was used to evaluate the coefficient of friction characteristics of Oils 3, 4, 5, 6, 7 and C. The test protocol used differed from that of Example 1, and is shown in Table 5 below. In Example 2, a stepped ramp temperature profile was followed, whereby each 600 seconds the temperature was raised by a step of 20 °C and held constant for 600 seconds until the next successive 20 °C ramp.

Table 5- HFRR Protocol

Contact	6 mm. Ball on 10 mm Disc
Load, N	3.9
Stroke Length, mm	1
Frequency, Hz.	20
Temperature range, °C	40-140
Temperature step, °C	20
Time between temperature steps, seconds	600

[0082] Results are expressed as average friction coefficient as a function of temperature and are summarised in Table 6 below, where the compositions tested are referred to as 3, 4, 5, 6, 7 and C in accordance with which additive component they contain. Each value is the average of two repeat tests.

Table 6

Temperature Stage (°C)	Composition					
	3	4	5	6	7	C
40	0.129	0.127	0.129	0.129	0.128	0.127
60	0.127	0.125	0.126	0.126	0.123	0.121
80	0.123	0.120	0.121	0.120	0.116	0.116
100	0.109	0.112	0.108	0.114	0.110	0.109
120	0.077	0.084	0.084	0.092	0.097	0.099
140	0.065	0.063	0.067	0.070	0.085	0.086

[0083] Table 6 shows that at lower temperature the friction coefficient decreases as the proportion of mono ester increases. Whereas, at higher temperatures, around 80 °C to 100 °C the Compositions 3 to 7 become comparable to Composition C. As temperature increases further, between 120 °C and 140 °C the results for Compositions 3 to 7 are superior to those of Reference Composition C.

Example 3

[0084] Additive component 8 was prepared comprising 53 mass% mono ester and 47 mass% diester. Component 8 was blended into a lubricating oil composition, by methods known in the art, to provide Composition 8 and Reference composition D. Compositions 8 and D each contained 0.3 mass % of Component 8 as active ingredient and identical customary amounts of an ashless dispersant, a metal detergent, an anti-oxidant, a zinc dihydrocarbyl dithiophosphate, and an antifoam. Composition 8 and Composition D differed in that Composition 8 comprised a tri-nuclear molybdenum additive providing 200 ppm by mass of molybdenum and Composition D comprised a di-nuclear molybdenum additive providing 200 ppm by mass of molybdenum

[0085] The high frequency reciprocating rig (HFRR) used in Example 1 was used to evaluate the coefficient of friction characteristics of Oils 8 and D. The test protocol used was the same as that used in Example 2, and as set out in Table 5 above.

[0086] Results are expressed as average friction coefficient as a function of temperature and are summarised in Table 7 below. Each value is the average of two repeat tests.

Table 7 Composition

Temperature Stage (°C)	8	D
40	0.127	0.130
60	0.121	0.126
80	0.116	0.119
100	0.108	0.112
120	0.101	0.105
140	0.080	0.100

[0087] It can be seen from Table 7 that at equivalent molybdenum content, the use of a tri-nuclear molybdenum source significantly reduces the friction coefficient compared to an equivalent composition comprising a di-nuclear molybdenum source.

Example 4

[0088] Two additive components were prepared consisting of various proportions of a monoester (glycerol mono-oleate), a diester (glycerol dioleate) and a triester (glycerol trioleate). The proportions, by mass %, of the mono, diester and triester are indicated in Table 8 below for each additive component.

Table 8

	Additive Component	
	9	10
Monoester	0	0
Diester	50	0
Triester	50	100

[0089] Each component was blended into a lubricating oil composition, by methods known in the art, to provide a fully formulated oil composition containing 0.3 mass % of the component as active ingredient and a molybdenum additive providing 200 ppm by mass of molybdenum, and identical customary amounts of an ashless dispersant, a metal detergent, an anti-oxidant, a zinc dihydrocarbyl dithiophosphate, and an antifoam.

[0090] The high frequency reciprocating rig (HFRR) of Example 1 was used to evaluate the coefficient of friction characteristics of Oils 9 and 10. The test protocol is the same as that used in Examples 2 and 3 and as shown in Table 5 above.

[0091] Results are expressed as average friction coefficient as a function of temperature and are summarised in Table 9 below, where the compositions tested are referred to as 9 and 10 in accordance with which additive component they contain.

Table 9 Composition

Temperature Stage (°C)	9	10
40	0.127	0.133
60	0.127	0.141
80	0.123	0.134
100	0.101	0.074
120	0.072	0.070

[0092] Table 9 shows that at higher temperatures, the composition comprising a greater proportion of triester is generally superior to the composition comprising a lower proportion of triester.

Claims

1. A composition comprising:

(A) an oil of lubricating viscosity;
(B) as an ester additive component, one or more esters of glycerol and a carboxylic acid containing 12 to 30 carbon atoms and 0 to 3 carbon-carbon double bonds wherein less than 50% by mass of the component is one or more monoesters; and
(C) as a further additive component, an oil-soluble molybdenum compound.

2. A composition as claimed in Claim 1, wherein 45 or less than, preferably 40 or less, such as 30 or less, % by mass of the ester additive component is one or more monoesters.

3. A composition as claimed in Claim 1 or Claim 2, wherein the carboxylic acid is a saturated or unsaturated C16 to C18 fatty acid, such as oleic acid.

4. A composition as claimed in Claim 1, 2 or 3, wherein the oil-soluble molybdenum compound is a trinuclear molybdenum compound.

5. A composition as claimed in any one of Claims 1 to 4, further comprising one or more co-additives, different from (B) and (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, metal dihydrocarbyl dithiophosphates, antioxidants, pour point depressants, additional friction modifiers, antifoam agents and viscosity modifiers.

6. A lubricating oil concentrate comprising:

(A) an oil of lubricating viscosity;
(B) as an ester additive component, one or more esters of glycerol and a carboxylic acid containing 12 to 30 carbon atoms and 0 to 3 carbon-carbon double bonds wherein less than 50% by mass of the component is one or more monoesters; and
(C) as a further additive component, an oil-soluble molybdenum compound.

7. A concentrate as claimed in Claim 6, wherein the oil of lubricating viscosity is present in an amount of from 30 to 70 mass%.

8. A method for improving the friction modification of an internal combustion engine at an operating temperature in excess of 90°C, comprising operating the engine and lubricating the engine with a composition as claimed in any one of Claims 1 to 5.

9. The use of an additive (B) in combination with an additive (C) as defined in any of Claims 1 to 4, for enhancing the friction-modification properties of a lubricating oil composition in the lubrication of an internal combustion engine at operating temperatures in excess of 90°C.

10. A composition comprising:

(A) an oil of lubricating viscosity;
(B) as an ester additive component, one or more esters of glycerol and a carboxylic acid containing 12 to 30 carbon atoms and 0 to 3 carbon-carbon double bonds wherein less than 55% by mass of the component is one or more monoesters; and
(C) as a further additive component, an oil-soluble tri-nuclear molybdenum compound.

11. A composition as claimed in Claim 10, wherein 50 or less than, preferably 45 or less, such as 40 or less or 30 or less, % by mass of the ester additive component is one or more monoesters.

12. A composition as claimed in Claim 10 or Claim 11, wherein the carboxylic acid is a saturated or unsaturated C16 to C18 fatty acid, such as oleic acid.

13. A composition as claimed in any of Claims 10 to 12, wherein the oil of lubricating viscosity is present in a concentrate-forming amount.

14. A composition as claimed in Claim 13, wherein the concentrate-forming amount is from 30 to 70 mass%.

15. A composition as claimed in any of Claims 10 to 14, further comprising one or more co-additives, different from (B) and (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, metal dihydrocarbyl dithiophosphates, antioxidants, pour point depressants, additional friction modifiers, antifoam agents and viscosity modifiers.

16. A method for improving the friction modification of an internal combustion engine at high temperature comprising operating the engine and lubricating the engine with a composition as claimed in any of Claims 10, 11, 12, and 15.

17. A method as claimed in Claim 16, wherein the high temperature is in excess of 90°C.

18. The use of an additive (B) in combination with an additive (C) as defined in any of Claims 10 or 12 for enhancing the high-temperature friction-modification properties of a lubricating oil composition in the lubrication of an internal combustion engine.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 10 9828

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CLASSIFICATION OF THE APPLICATION (IPC)
C10M141/02 C10M141/08 C10M141/10 C10M163/00

TECHNICAL FIELDS SEARCHED (IPC)
C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	9 February 2006	Dötterl, E

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