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(54) **A lubricating oil composition**

(57) A crankcase lubricating oil composition comprising (A) an oil of lubricating viscosity; and (B) as an additive component one or more oil-soluble organic acid anhydrides, the or each anhydride carrying at least one linear

(unbranched) aliphatic hydrocarbyl substituent having 12 to 36 carbon atoms.

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**Description****FIELD OF THE INVENTION**

5 **[0001]** The present invention relates to automotive lubricating oil compositions, more especially to automotive lubricating oil compositions for use in piston engines, especially gasoline (spark-ignited) and diesel (compression-ignited) crankcase lubrication, such compositions being referred to as crankcase lubricants. In particular, although not exclusively, the present invention relates to use of additives with friction modification properties in automotive lubricating oil compositions.

**BACKGROUND OF THE INVENTION**

10 **[0002]** A crankcase lubricant is an oil used for general lubrication in an internal combustion engine where an oil sump is situated generally 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.

15 **[0003]** Friction modifiers, also referred to as friction-reducing agents, may be boundary additives that operate by lowering friction coefficient and hence improve fuel economy; the art describes use of glycerol monoesters as friction modifiers, for example in US-A-4,495,088; US-A-4,683,069; EP-A-0 092 946; and WO-A-01/72933. Glycerol monoester friction modifiers have been and are used commercially.

20 **[0004]** Lubricant specifications are becoming more exacting. For example, passenger car motor oil (PCMO) specifications have or will require more stringent fuel economy performance, such as in respect of improved fuel economy retention. Known friction modifiers such as glycerol monoesters may not be able to meet those requirements at moderate treat rates.

25 **[0005]** The art describes chemistries other than glycerol monoesters as having friction modification properties. For example, US-A-5,840,662 ('662) describes, as a friction modifier, a succinic anhydride that is mono-substituted with a depicted C<sub>6</sub> to C<sub>30</sub> isomerized alkenyl group, or its fully saturated alkyl analog. '662 is mainly concerned with power transmitting fluids but briefly alludes to applicability to "a wide variety of lubricating oils (e.g. , crankcase engine oils, etc.)". '662 makes no mention of fuel economy retention.

**SUMMARY OF THE INVENTION**

30 **[0006]** The present invention meets the above problem by providing, as crankcase lubricant friction modifiers, certain organic acid anhydrides carrying aliphatic hydrocarbyl groups. In contrast to the anhydrides of '662, the hydrocarbyl groups are linear (i.e. unbranched). The data in this specification demonstrate solution of the technical problem in the prior art and enhanced performance of compounds with linear substituent groups as opposed to branched substituent groups.

35 **[0007]** In accordance with a first aspect, the present invention provides a crankcase lubricating oil composition comprising or made by admixing

40 (A) an oil of lubricating viscosity; and

(B) as an additive component, one or more oil-soluble organic acid anhydrides, the or each anhydride carrying at least one linear unbranched aliphatic hydrocarbyl group having 12 to 36, such as 12 to 24, carbon atoms.

45 **[0008]** According to a second aspect, the present invention provides a method of enabling a passenger car motor oil composition to achieve a reduced boundary friction coefficient when the oil is fresh and to retain that boundary friction performance under oxidative conditions, which method comprises providing the composition with minor amounts of one or more additives (B) as defined in the first aspect of the invention. The oil may meet the viscosity-dependent fuel economy specifications of GF-4 as measured on the sequence VIB engine test.

50 **[0009]** According to a third aspect, the present invention provides a method of lubricating surfaces of an internal combustion engine during its operation comprising:

(i) providing, in a minor amount, one or more additives (B) as defined in the first aspect of the invention in a major amount of an oil of lubricating viscosity to make a lubricant, to improve the friction modifying properties of the lubricant;

55 (ii) providing the lubricant to the crankcase of the internal combustion engine;

(iii) providing a hydrocarbon fuel in the combustion chamber of the engine; and

(iv) combusting the fuel in the combustion chamber.

**[0010]** In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

5 "active ingredient" 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;

10 "hydrocarbyl" means a chemical group of a compound that contains only hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom;

15 "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;

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

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

25 "TBN" means total base number as measured by ASTM D2896;

"phosphorus content" is measured by ASTM D5185;

30 "sulfur content" is measured by ASTM D2622; and

"sulfated ash content" is measured by ASTM D874.

35 **[0011]** 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.

**[0012]** Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

40 **[0013]** Furthermore, the constituents of this invention may be isolated or be present within a mixture and remain within the scope of the invention.

#### **DETAILED DESCRIPTION OF THE INVENTION**

45 **[0014]** The features of the invention relating, where appropriate, to each and all aspects of the invention, will now be described in more detail as follows:

#### **OIL OF LUBRICATING VISCOSITY (A)**

50 **[0015]** 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). Also, a base oil is useful for making concentrates as well as for making lubricants therefrom.

**[0016]** A base oil 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<sup>2</sup>s<sup>-1</sup> at 100°C.

55 **[0017]** 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.

5 **[0018]** 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.

10 **[0019]** 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, sebacic 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.

15 **[0020]** Esters useful as synthetic oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

20 **[0021]** 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 which 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 removing spent additive and oil breakdown products.

25 **[0022]** 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<sub>2</sub> 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.

30 **[0023]** Base oil may be categorised in Groups I to V according to the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998; 1509 definition.

35 **[0024]** When the oil of lubricating viscosity is used to make a concentrate, it is present in a concentrate-forming amount (e.g., from 30 to 70, such as 40 to 60, mass %) to give 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 component (B) above, optionally with one or more co-additives. 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.

40 **[0025]** Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additives in lubricants. When preparing a lubricant that contains more than one type of additive (sometimes 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 one or more co-additives, such as described hereinafter, in a single concentrate.

45 **[0026]** To obtain a crankcase lubricant, the oil of lubricating viscosity may be provided in a major amount, in combination with a minor amount of additive component (B) as defined herein and, if necessary, one or more co-additives, such as described hereinafter. This may be done 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 before, at the same time as, or after addition of other additives.

50 **[0027]** Preferably, the oil of lubricating viscosity is present in the lubricant in an amount of greater than 55 mass %, more preferably greater than 60 mass %, even more preferably greater than 65 mass %, based on the total mass of the lubricant. Preferably, the oil of lubricating viscosity is present in an amount of less than 98 mass %, more preferably less than 95 mass %, even more preferably less than 90 mass %, based on the total mass of the lubricant.

55 **[0028]** The terms "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.

**[0029]** The lubricants of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited or compression-ignited two- or four-stroke reciprocating engines, by adding the lubricant thereto.

**[0030]** The lubricating oil compositions of the invention comprise defined components that may or may not remain the same chemically before and after mixing with an oleaginous carrier. This invention encompasses compositions which comprise the defined components before mixing, or after mixing, or both before and after mixing.

**[0031]** When concentrates are used to make the lubricants, they may for example be diluted with 3 to 100, e.g. 5 to 40, parts by mass of oil of lubricating viscosity per part by mass of the concentrate.

**[0032]** The lubricants of the present invention may contain low levels of phosphorus, namely not greater than 0.09 mass %, preferably up to 0.08 mass %, more preferably up to 0.06 mass % of phosphorus, expressed as atoms of phosphorus, based on the total mass of the lubricant.

**[0033]** Typically, the lubricants may contain low levels of sulfur. Preferably, the lubricant contains up to 0.4, more preferably up to 0.3, most preferably up to 0.2, mass % sulfur, expressed as atoms of sulfur, based on the total mass of the lubricant.

**[0034]** Typically, the lubricant may contain low levels of sulfated ash. Preferably, the lubricant contains up to 1.0, preferably up to 0.8, mass % sulfated ash, based on the total mass of the lubricant.

**[0035]** Suitably, the lubricant may have a total base number (TBN) of between 4 to 15, preferably 5 to 11.

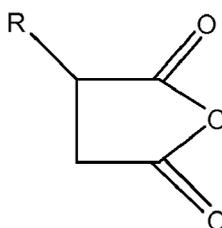
## ADDITIVE COMPONENT (B)

**[0036]** In (B), the organic acid anhydrides are anhydrides of carboxylic acids and may be cyclic or linear. The cyclic anhydrides may be aliphatic such as anhydrides of dicarboxylic acids, for example having a two-carbon atom chain separating the carboxyl groups, particular examples of the anhydrides being succinic anhydride and maleic anhydride; or the cyclic anhydrides may be aromatic for example phthalic anhydride. The linear anhydrides may be symmetrical anhydrides of monocarboxylic acids or mixed anhydrides of different monocarboxylic acids.

**[0037]** Without wishing to be bound by any theory, it is believed that the anhydrides, in operation in lubricants and to achieve the performance benefits described herein, are convertible to carboxylic acids carrying at least one said aliphatic hydrocarbyl substituent group.

**[0038]** Each anhydride, as stated, carries at least one linear (unbranched) aliphatic hydrocarbyl group having 12 to 36, such as 12 to 24, carbon atoms. For example, the hydrocarbyl group may be saturated, i.e. be an alkyl group, or be a double-bond unsaturated hydrocarbyl group having one or more sources of unsaturation, preferably an alkenyl group. Preferably, the or each anhydride is mono-substituted with an aliphatic hydrocarbyl group. When di-substituted, the substituent groups are independent.

**[0039]** Preferably, (B) is a succinic anhydride, and as an example of (B), there may be mentioned a substituted succinic anhydride of the formula:



where R is a linear (unbranched) aliphatic hydrocarbyl group having 12 to 36 carbon atoms.

**[0040]** In a preferred example, the hydrocarbyl substituent or R is n-octadecyl.

**[0041]** Acid anhydrides useful in the present invention may be commercially available or may be made by methods known to those skilled in the art.

**[0042]** Suitably, the additive component (B) is present in an amount of 0.1 to 10, preferably 0.1 to 5, more preferably 0.1 to 2, mass % of the lubricant, based on the total mass of the lubricant.

## CO-ADDITIVES

**[0043]** Co-additives, with representative effective amounts in lubricants, that may also be present, different from

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additive component (B), are listed below. All the values listed are stated as mass percent active ingredient.

	<b>Additive</b>	<b>Mass %</b>	<b>Mass %</b>
		(Broad)	(Preferred)
5	Ashless Dispersant	0.1 - 20	1 - 8
	Metal Detergents	0.1 - 15	0.2 - 9
	Friction modifier	0 - 5	0 - 1.5
	Corrosion Inhibitor	0 - 5	0 - 1.5
10	Metal Dihydrocarbyl Dithiophosphate	0 - 10	0 - 4
	Anti-Oxidants	0 - 5	0.01 - 3
	Pour Point Depressant	0.01 - 5	0.01 - 1.5
	Anti-Foaming Agent	0 - 5	0.001 - 0.15
15	Supplement Anti-Wear Agents	0 - 5	0 - 2
	Viscosity Modifier (1)	0 - 6	0.01 - 4
	Mineral or Synthetic Base Oil	Balance	Balance

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

**[0044]** The final lubricant, 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 additives, i.e. (B) and any co-additives, the remainder being oil of lubricating viscosity.

**[0045]** 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.

**[0046]** 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. 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.

**[0047]** 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 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.

**[0048]** 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<sub>4</sub> refinery stream.

**[0049]** 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 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.

**[0050]** 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.

**[0051]** 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 when 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 reaction of 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.

**[0052]** 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.

**[0053]** Particularly preferred metal detergents are neutral and overbased alkali or alkaline earth metal salicylates having a TBN of from 50 to 450, preferably a TBN of 50 to 250. Highly preferred salicylate detergents include alkaline earth metal salicylates, particularly magnesium and calcium, especially, calcium salicylates.

**[0054]** Friction modifiers 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; oxazoline compounds; and alkoxyated alkylsubstituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

**[0055]** 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. Suitable oil-soluble organo-molybdenum compounds have a molybdenum-sulfur core. As examples there may be mentioned dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates. The molybdenum compound is dinuclear or trinuclear.

**[0056]** One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is trinuclear molybdenum compounds of the formula  $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$  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.

**[0057]** The molybdenum compounds may be present in a lubricating oil composition at a concentration in the range 0.1 to 2 mass %, or providing at least 10 such as 50 to 2,000 ppm by mass of molybdenum atoms.

**[0058]** Preferably, the molybdenum from the molybdenum compound is present in an amount of from 10 to 1500, such as 20 to 1000, more preferably 30 to 750, ppm based on the total weight of the lubricant. For some applications, the molybdenum is present in an amount of greater than 500 ppm.

**[0059]** Anti-oxidants are sometimes referred to as oxidation inhibitors; they increase the resistance of the lubricant 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 evidenced by sludge in the lubricant, varnishlike 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., organosulfur 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, sulfur-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, zinc molybdenum, manganese, nickel or copper. Zinc salts are most commonly used in lubricants such as in amounts of 0.1 to 10, preferably 0.2 to 2, mass %, based upon the total mass of the lubricant. 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  $\text{P}_2\text{S}_5$ , and then neutralising the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reaction with mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one acid are entirely secondary in character and the hydrocarbyl groups on the other acids 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 sulfur 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.

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

[0066] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the oil will flow or can be poured. Such additives are well known. Typical of these additive are C<sub>8</sub> to C<sub>18</sub> dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

[0067] Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane, can provide foam control.

[0068] 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 reaction of a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

[0069] Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricant. 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.

[0070] 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

[0071] The invention will now be particularly described in the following examples which are not intended to limit the scope of the claims hereof.

[0072] The following friction modifiers were tested:-

n-octadecen-2-yl succinic anhydride ("nODSA"),

n-octadecyl succinic anhydride ("2H-nODSA"),

n-iso-octadecen-2-yl succinic anhydride ("isoODSA"),

polyisobutene succinic anhydride (C<sub>17</sub> straight chain) ("PIBSA"),

[0073] Each of the nODSA, 2H-nODSA and isoODSA were commercially available materials. PIBSA was made by known methods.

[0074] Each of the above friction modifiers was blended separately into a lubricating oil composition (Oil A) at a treat rate of 0.5 wt % to give a set of test lubricants. Apart from the identity of the friction modifier, each lubricant was the same and comprised an adpack consisting of detergents, antifoam, dispersants, antioxidant and diluent blended with a viscosity modifier, pour point depressant, base stock and the friction modifier.

## TESTING AND RESULTS

### Fresh Oil HFRR Testing

[0075] A high frequency reciprocating rig ("HFRR") was used to evaluate the coefficient of friction of certain of the above lubricants. Experimentation was carried out using a step ramp profile: coefficient of friction was measured for 5 minutes at each temperature as the temperature was increased from 40°C to 140° at 20°C intervals. A 4 N load was applied via a 400 g weight and the upper specimen reciprocated over a distance of 1 mm at a frequency of 40 Hz.

[0076] Table 1 below sets out results of a first set of experiments. It gives a representative average coefficient of friction value at each temperature.

TABLE 1

Temp (°C):	40	60	80	100	120	140
Oil A	142	144	148	159	166	163
* Oil A+ 2H-nODSA (0.5 wt %)	118	113	110	105	97	89
Oil A+ isoODSA (0.5 wt %)	136	135	130	126	119	110

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[0077] Values given are friction coefficient ( $\times 10^3$ ), lower values indicating better performance.

[0078] The values demonstrate that the 2H-nODSA-containing lubricant (of the invention and indicated by an asterisk) is better than the isoODSA-containing lubricant (a comparison, representative of the prior art), both at the same treat rate.

[0079] Table 2 below sets out results of a second set of experiments in the same way as in Table 1 (treat rates are 0.5 wt %).

TABLE 2

Temp (°C):	40	60	80	100	120	140
Oil A	142	144	145	163	173	171
* Oil A+ 2H-nODSA	117	115	112	107	106	103
* Oil A+ nODSA	120	125	119	113	105	95
Oil A+ PIBSA	139	148	143	139	140	140

[0080] The values demonstrate that both of the 2H-nODSA- and nODSA-containing lubricants (of the invention and indicated by asterisks) are better than Oil A alone and Oil A and PIBSA, thereby demonstrating the friction modifying properties of the additives of the invention.

### Aged Oil Testing

[0081] Certain of the above lubricants were aged using the CEC L-48-B test procedure running at 150°C for 50 hours. Aliquots were sampled from the CEC L-48-B test apparatus after 8, 24, 30 and 50 hours of running time, and then tested on the HFRR as described above for boundary friction performance. Table 3 below summarises coefficient of friction values thereby attained for each lubricant at 140°C over the duration of the CEC L-48-B ageing procedure (treat rates are 0.5 wt %).

TABLE 3

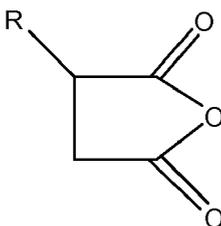
Ageing Time (hours)	0	8	24	30	50
Oil A	171	167	157	165	159
* Oil A+ 2H-nODSA	103	95	97	96	148
* Oil A+ nODSA	95	131	153	154	150
Oil A+ PIBSA	140	161	157	157	155

[0082] The figures show that 2H-nODSA gives rise to superior boundary friction reducing durability in comparison with the control in the HFRR when subjected to oxidative conditions. Also, they show that the 2H-nODSA-containing lubricant retains friction modifying efficiency over the initial 30 hours of the test. This is a clear demonstration that the 2H-nODSA-containing lubricant retains friction modifier efficiency under oxidative conditions.

### Claims

1. A crankcase lubricating oil composition comprising or made by admixing
  - (A) an oil of lubricating viscosity; and
  - (B) as an additive component, one or more oil-soluble organic acid anhydride, the or each anhydride carrying at least one linear unbranched aliphatic hydrocarbyl substituent having 12 to 36, such as 12 to 24, carbon atoms.
2. A composition as claimed in claim 1 where the or each hydrocarbyl substituent is a saturated or double-bond unsaturated hydrocarbyl group.
3. A composition as claimed in claim 2 where the hydrocarbyl substituent is an alkyl group.
4. A composition as claimed in any of claims 1 to 3 where the acid anhydride is succinic anhydride.

5. A composition as claimed in claim 4 where the succinic anhydride has the formula:



where R is a linear unbranched aliphatic hydrocarbyl substituent having 12 to 36 carbon atoms.

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6. A composition as claimed in claim 5 wherein R is an alkyl group.
7. A composition as claimed in any of claims 1 to 6 where the or each aliphatic hydrocarbyl group is n-octadecyl.
8. A composition as claimed in any of claims 1 to 7 where the oil of lubricating viscosity is present in a concentrate-forming amount.
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9. A composition as claimed in claim 8 further including one or more other additive components, different from (B).
10. A composition as claimed in any of claims 1 to 7 in the form of a lubricant where the oil of lubricating viscosity is present in a major amount and (B), and any other additive components, are present in respective minor amounts.
- 25
11. A composition as claimed in claim 10 where the other additives, different from (B), are selected from one or more ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam and viscosity modifiers.
- 30
12. A method of enabling a passenger car motor oil composition to achieve a reduced boundary friction coefficient when the oil is fresh and to retain that boundary friction performance under oxidative conditions, which method comprises providing the composition with minor amounts of one or more additives (B) as defined in any of claims 1 to 7.
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13. A method of lubricating surfaces of an internal combustion engine during its operation comprising:
- (i) providing, in a minor amount, one or more additives (B) as defined in any of claims 1 to 7 in a major amount of an oil of lubricating viscosity to make a lubricant, to improve the friction modifying properties of the lubricant;
- (ii) providing the lubricant to the crankcase of the internal combustion engine;
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- (iii) providing a hydrocarbon fuel in the combustion chamber of the engine; and
- (iv) combusting the fuel in the combustion chamber.
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EUROPEAN SEARCH REPORT

Application Number  
EP 10 19 1164

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