



(11) **EP 1 783 198 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
09.05.2007 Bulletin 2007/19

(51) Int Cl.:
C10M 167/00 *(2006.01)* **C10N 30/06** *(2006.01)*

(21) Application number: **06122139.6**

(22) Date of filing: **11.10.2006**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**
Designated Extension States:
AL BA HR MK YU

(30) Priority: **03.11.2005 EP 05270076**

(71) Applicant: **Infineum International Limited
Abingdon,
Oxfordshire OX13 6BB (GB)**

(72) Inventor: **Scott, Robin Howard,
c/o Infineum UK Ltd.
Abingdon, Oxon, OX13 6BB (GB)**

(74) Representative: **Goddard, Frances Anna
Infineum UK Ltd.
P.O. Box 1
Milton Hill Business &
Technology Centre
Abingdon, Oxfordshire OX13 6BB (GB)**

(54) **Linear diblock copolymers as anti-wear additives for lubricants of internal combustion engine crankcases**

(57) An internal combustion engine crankcase lubricating oil composition has a phosphorus content of not greater than 0.09 mass %, a metal detergent additive system comprising one or more metal salts of organic carboxylic acids, and a viscosity index improver compris-

ing a linear diblock copolymer, one block being derived from a vinyl aromatic hydrocarbon monomer and one block being derived from a diene monomer.

EP 1 783 198 A2

Description

[0001] This invention relates to internal combustion engine crankcase lubricating oil compositions (or lubricants), more especially to compositions suitable for use in piston engine, especially for gasoline (spark-ignited) and diesel (compression-ignited) piston engine lubrication; and to use of additives in such compositions for reducing wear.

[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.

[0003] There has been a need and/or requirement to reduce the level of phosphorus in crankcase lubricants in order to improve the durability of exhaust gas treatment catalysts. Reductions in the amount of phosphorus-containing lubricant additives can, however, cause increased wear in the engine.

[0004] It is also known to provide salicylate-based metal detergents as additives in crankcase lubricants.

[0005] EP-A-1 338 643 ('643) describes crankcase lubricants that contain overbased calcium or magnesium salicylate and that have less than 50 ppm of phosphorus. '643 describes tests on an example of such a lubricant, containing calcium salicylate and having no phosphorus, to measure the average cam wear, which is reported to be within ILSAC GF-3 engine test limits.

[0006] A problem in '643 is that the formulations therein may exhibit poor cam and lifter wear. Cam-plus-lifter wear is one of the parameters of the sequence IIIG test, which is an API Category SM, ILSAC Category GF-4 test carried out during high temperature conditions and which simulates high-speed service during relatively high ambient temperature conditions.

[0007] The present invention, surprisingly, and as evidenced by the data presented in this specification, overcomes the problem by employing formulations that contain specific viscosity index improvers.

[0008] In a first aspect, the invention provides an internal combustion engine crankcase lubricating oil composition having a phosphorus concentration, expressed as atoms of phosphorus, of not greater than 0.09 mass %, based on the mass of the oil composition, which composition comprises or is made by admixing:

- (A) an oil of lubricating viscosity, in a major amount;
- (B) a metal detergent system, as an additive in a minor amount, comprising one or more metal salts of organic carboxylic acids; and
- (C) a viscosity index improver comprising a linear diblock copolymer comprising at least one block derivable primarily from a vinyl aromatic hydrocarbon monomer and at least one block derivable primarily from a diene monomer.

[0009] In a second aspect, the invention provides a method of lubricating a compression-ignited or spark-ignited internal combustion engine, which method comprises supplying to the engine a lubricating oil composition according to the first aspect of the invention.

[0010] In a third aspect, the invention provides the use of a viscosity index improver as defined in the first aspect of the invention, to improve the cam and lifter wear in the crankcase lubrication of an internal combustion engine by a lubricating oil composition having a phosphorus concentration, expressed as atoms of the phosphorus, of not greater than 0.08 mass % based on the mass of the lubricating oil composition.

[0011] A lubricating oil composition according to the present invention may have a phosphorus content of at least greater than 0.005, preferably at least 0.01, and not greater than 0.08 mass %, based on the mass of the oil composition.

[0012] A lubricating oil composition according to the present invention may have a total base number (TBN) of between 2 and 9, preferably between 4 and 8.

[0013] Preferably, the lubricating oil composition of the invention is a low viscosity oil composition, such as a multigrade oil composition satisfying the SAE 0W-X or SAE 5W-X characteristics where X represents, for example, any one of 20, 30 and 40.

[0014] In this specification, the following words and expressions, if and when used, shall have the meanings ascribed below:

- "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;
- "major amount" means in excess of 50 mass % of a composition;
- "minor amount" means less than 50 mass % of a composition;
- "TBN" means total base number as measured by ASTM D2896.

[0015] Furthermore in this specification:

"phosphorus content" is as measured by ASTM D5185;

"sulphated ash content" is as measured by ASTM D874;

"sulphur content" is as measured by ASTM D2622;

"KV 100" means kinematic viscosity at 100°C as measured by ASTM D445.

[0016] 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.

[0017] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0018] 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)

[0019] This, sometimes referred to as the base oil or base stock, is the primary liquid constituent of the composition into which additives and possibly other oils are blended.

[0020] 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, mm²s⁻¹ at 100°C.

[0021] 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.

[0022] 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 derivatives, analogues and homologues thereof.

[0023] 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.

[0024] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0025] 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 approval of spent additive and oil breakdown products.

[0026] 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 hydrogen and carbon monoxide 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.

[0027] Base oil may be categorised in Groups I to V according to the API EOLCS 1509 definition. Base oil derived from one or more of Groups III, IV and V is preferred.

[0028] The oil of lubricating viscosity is provided in a major amount, in combination with minor amounts of the additives (B) and (C) and, if necessary, one or more co-additives such as described hereinafter, constituting the 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.

[0029] 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. They 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.

Metal Detergent System (B)

[0030] Metal detergents are additives that reduce formation of piston deposits in engines and that may have acid-neutralising properties, and the term 'detergent' is used herein to define a material capable of providing either or both of these functions within the lubricating oil composition. They are based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants, and that generally comprise a polar head with a long hydrophobic tail.

[0031] As stated, the metal detergent system comprises one or more metal salts or organic carboxylic acids.

[0032] Preferably the carboxylic acids are aromatic carboxylic acids; more preferably salts of aromatic carboxylic acids constitute all of the metal detergent systems.

[0033] The aromatic moiety of the aromatic carboxylic acids can contain hetero atoms such as nitrogen and oxygen but preferably contains only carbon and hydrogen atoms, for example six or more carbon atoms. Benzene is a preferred moiety.

[0034] The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges.

[0035] The carboxylic moiety may be attached directly or indirectly to the aromatic moiety, preferably directly to a carbon atom on the aromatic moiety, such as a carbon atom on a benzene ring.

[0036] More preferably, the aromatic moiety also contains a second functional group such as a hydroxyl group, attached directly or indirectly to a carbon atoms on the aromatic moiety.

[0037] Preferred examples of aromatic carboxylic acids are salicylic acids such as hydrocarbyl-substituted salicylic acids. "Hydrocarbyl" means groups containing substantially hydrogen and carbon atoms and bonded to the remainder of the molecule directly via a carbon atoms; they may contain one or more hetero atoms provided these do not detract from the essentially hydrocarbyl nature of the group.

[0038] The salts may be complexed with other surfactants such as phenates and may be in the form of hydroxybenzoates. Alkylphenols may be present. US-A-5 808 145; EP-A-0 933 417 and EP-A-0 985 726 describe examples of such complexes.

[0039] The metal is preferably an alkaline earth metal such as calcium and magnesium.

[0040] Another class of useful metal salts of organic carboxylic acids are metal salts of linear and cyclic compounds containing phenol and salicylic acid units, sometimes referred to as "salicylic calixarenes". Such detergents are described, for example, in EP-A-0 708 171; WO 99/0 025 677; WO 02/0 072 529; and WO 03/0 018 728.

[0041] Where the aromatic carboxylic acid is salicylic acid, conveniently, each salicylate is alkyl-substituted for example with independent alkyl groups having from 8 to 30 carbon atoms and which may be linear, branched or cyclic. As examples of alkyl groups there may be mentioned the following: octyl, nonyl, decyl, dodecyl, pentadecyl, octadecyl, eicosyl, docosyl, tricosyl, hexacosyl, triacontyl, dimethylcyclohexyl, ethylcyclohexyl, methylcyclohexylmethyl and cyclohexylethyl.

[0042] Preferably, substantially all of the metal detergent system is calcium salicylate in the sense that it contains, at most, minor or adventitious amounts of metal detergents other than the calcium salicylate. More preferred is a metal detergent system from which metal phenates and metal sulfonates are substantially, or more preferably completely, absent.

[0043] Conveniently, calcium salicylate, when used, provides from 50 to 4,000 preferably from 100 to 3,000, ppm by mass of atoms of calcium, based on the mass of the lubricating oil composition.

[0044] The detergent additive(s) in the detergent system may be neutral or overbased, preferably overbased. Conveniently, they may have a TBN in the range of 15 or 60 to 600, preferably 100 to 450.

Viscosity Index Improvers (C)

[0045] Viscosity Index Improvers, or VI Improvers, useful in the practice of the present invention are linear diblock copolymers that comprise at least one block derived primarily from a vinyl aromatic hydrocarbon monomer, and at least

one block derived primarily from a diene monomer. Useful vinyl aromatic hydrocarbon monomers include those containing from 8 to 16 carbon atoms such as aryl-substituted styrenes, alkoxy-substituted styrenes, vinyl naphthalene, alkyl-substituted vinyl naphthalenes and the like. Dienes, or diolefins, contain two double bonds, commonly located in conjugation in a 1,3 relationship. Olefins containing more than two double bonds, sometimes referred to as polyenes, are also considered within the definition of "diene" as used herein. Useful dienes include those containing from 4 to about 12 carbon atoms, preferably from 8 to 16 carbon atoms, such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, 4,5-diethyl-1,3-octadiene, with 1,3-butadiene and isoprene being preferred.

[0046] Linear block copolymers useful in the practice of the present invention may be represented by the following general formula:



wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer; and
B is a polymeric block derived predominantly from conjugated diene monomer.

[0047] Also included in the definition of "linear diblock copolymers" are tapered linear block copolymers represented by the following general formula:



wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;
B is a polymeric block derived predominantly conjugated diolefin monomer; and
A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

[0048] As used herein in connection with polymer block composition, "predominantly" means that the specified monomer or monomer type that is the principle component in that polymer block is present in an amount of at least 85% by weight of the block.

[0049] 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.

[0050] The block copolymers may include mixtures of linear polymers as disclosed above, having different molecular weights and/or different vinyl aromatic contents as well as mixtures of linear diblock copolymers having different molecular weights and/or different vinyl aromatic contents. The use of two or more different polymers may be preferred to a single polymer depending on the rheological properties the product is intended to impart when used to produce formulated engine oil.

[0051] The block copolymer may have a number average molecular weight of between 200,000 and 1,500,000. A number average molecular weight of between 350,000 and 900,000 is preferred. The amount of vinyl aromatic content of the copolymer is preferably between 5% and 40% by weight of the copolymer. For such copolymers, number average molecular weights between 85,000 and 300,000 are acceptable.

[0052] Useful block copolymers include those prepared in bulk, suspension, solution or emulsion. As is well known, polymerization of monomers to produce hydrocarbon polymers may be accomplished using free-radical, cationic and anionic initiators or polymerization catalysts, such as transition metal catalysts used for Ziegler-Natta and metallocene type (also referred to as "single-site") catalysts.

[0053] Preferably, the linear diblock copolymer is at least one linear diblock copolymer having a polystyrene block and a block derived from isoprene, butadiene, or a mixture thereof. More preferably, the linear diblock copolymer is at least one linear diblock copolymer selected from hydrogenated styrene/butadiene diblock copolymers and hydrogenated styrene/isoprene diblock copolymers. Preferably, the diblock copolymer has a Shear Stability Index value, determined in accordance with the procedure of ASTM D6278-98 (known as the Kurt-Orban (KO) or DIN bench test), of from 2 to

50%, more preferably from 5 to 50% (30 cycles), and the block of the diblock copolymer derived from diene comprises from 40 to 90 mass % derived from isoprene and from 10 to 60 mass % derived from butadiene.

[0054] Optionally, VI improvers used in the practice of the invention can be provided with nitrogen-containing functional groups that impart dispersant capabilities to the VI improver. One trend in the industry has been to use such "multifunctional" VI improvers in lubricants to replace some or all of the dispersant. Nitrogen-containing functional groups can be added to a polymeric VI improver by grafting a nitrogen- or hydroxyl- containing moiety, preferably a nitrogen-containing moiety, onto the polymeric backbone of the VI improver (functionalizing). Processes for the grafting of a nitrogen-containing moiety onto a polymer are known in the art and include, for example, contacting the polymer and nitrogen-containing moiety in the presence of a free radical initiator, either neat, or in the presence of a solvent. The free radical initiator may be generated by shearing (as in an extruder) or heating a free radical initiator precursor, such as hydrogen peroxide.

[0055] The amount of nitrogen-containing grafting monomer will depend, to some extent, on the nature of the substrate polymer and the level of dispersancy required of the grafted polymer. To impart dispersancy characteristics to both star and linear copolymers, the amount of grafted nitrogen-containing monomer is suitably between 0.4 and 2.2 wt. %, preferably from 0.5 to 1.8 wt. %, most preferably from 0.6 to 1.2 wt. %, based on the total weight of grafted polymer.

[0056] Methods for grafting nitrogen-containing monomer onto polymer backbones, and suitable nitrogen-containing grafting monomers are known and described, for example, in U.S. Patent No. 5,141,996, WO 98/13443, WO 99/21902, U.S. Patent No. 4,146,489, U.S. Patent No. 4,292,414, and U.S. Patent No. 4,506,056. (See also J Polymer Science, Part A: Polymer Chemistry, Vol. 26, 1189-1198 (1988); J. Polymer Science, Polymer Letters, Vol. 20, 481-486 (1982) and J. Polymer Science, Polymer Letters, Vol. 21, 23-30 (1983), all to Gaylord and Mehta and Degradation and Crosslinking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides; J. Applied Polymer Science, Vol. 33, 2549-2558 (1987) to Gaylord, Mehta and Mehta.

[0057] Diblock copolymer components of the present invention are available as commercial products. Examples of commercially available styrene/hydrogenated isoprene linear diblock copolymers include Infineum SV140™, Infineum SV150™ and Infineum SV160™, available from Infineum USA L.P. and Infineum UK Ltd.; Lubrizol® 7318, available from The Lubrizol Corporation; and Septon 1001™ and Septon 1020™, available from Septon Company of America (Kuraray Group). Suitable styrene/1, 3-butadiene hydrogenated block copolymers are sold under the tradename Gliss-oviscal™ by BASF.

[0058] The viscosity index improver may, for example, be provided in an amount from 0.01 to 20, preferably 1 to 10, mass % based on the mass of the lubricating oil composition.

Other Additives

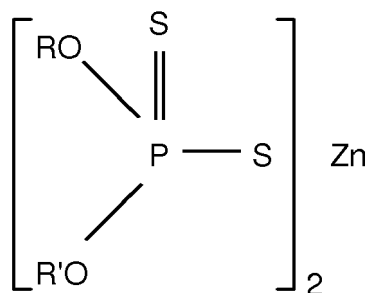
[0059] Other additives, such as the following, may also be present in the lubricating oil compositions of the present invention.

[0060] Ashless dispersants comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersants may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and a polyalkylene polyamine.

[0061] Anti-wear agents may comprise dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc.

[0062] Dihydrocarbyl dithiophosphate metal salts 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 P₂S₅ and then neutralizing the formed DDPA with a metal 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 metal salt, any basic or neutral metal compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of metal due to the use of an excess of the basic metal compound in the neutralization reaction.

[0063] The preferred zinc dihydrocarbyl dithiophosphates (ZDDP) are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbonyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butyl-phenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbonyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates.

[0064] To limit the amount of phosphorus introduced into the lubricating oil composition by ZDDP to no more than 0.09 mass %, the ZDDP should preferably be added to the lubricating oil compositions in amounts no greater than from about 1.1 to 1.3 mass %, based upon the total mass of the lubricating oil composition.

[0065] Oxidation inhibitors or antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, aromatic amines, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfides, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorus esters, metal thiocarbamates and oil-soluble copper compounds as described in U.S. 4,867,890.

[0066] Friction Modifiers which include boundary lubricant additives that lower friction coefficient and hence improve fuel economy may be used. Examples include ester-based organic friction modifiers such as partial fatty acid esters of polyhydric alcohols, for example, glycerol monooleate; and amine-based organic friction modifiers. Further examples are additives that deposit molybdenum disulphide such as organo-molybdenum compounds where the molybdenum is, for example, in dinuclear or trinuclear form.

[0067] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0068] Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 mass % active ingredient.

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

[0070] 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 additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0071] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0072] Lubricating oil compositions of the present invention may optionally also contain VI improving materials other than Viscosity Index Improvers (C), such as ethylene-propylene, or other olefin copolymer (OCP) VI improvers, or random or linear triblock copolymers or random star or star block copolymers derived from vinyl aromatic hydrocarbon and diene. Such other VI improvers are well known and available commercially. Preferably, Viscosity Index Improvers (C) are the sole VI improvers used in the lubricating oil composition.

[0073] The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the components can be added directly to the base stock or base oil blend by dispersing or dissolving it in the base stock or base oil blend at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

[0074] Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate described herein as the additive package, which is subsequently blended into base stock to make the finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of a base lubricant.

[0075] The concentrate is preferably made in accordance with the method described in US 4,938,880.

[0076] The final crankcase lubricating oil composition may employ from 2 to 20, preferably 4 to 18, and most preferably 5 to 17, mass % of the concentrate or additive package with the remainder being base stock. Preferably, lubricating oil compositions of the present invention have a sulphated ash concentration of not greater than 1.0 mass % and/or a sulphur concentration, expressed as atoms of sulphur, of not greater than 0.3, more preferably not greater than 0.2, mass %.

Engines

[0077] The invention is applicable to a range of internal combustion engines such as compression-ignited and spark-ignited two-or four-stroke reciprocating engines. Examples include engines for power-generation, locomotive and marine equipment and heavy duty on-highway trucks; heavy duty off-highway engines such as may be used for agriculture, construction and mining and engines for light duty commercial and passenger car applications.

Examples

[0078] The invention will now be particularly described in the following examples which are not intended to limit the scope of the claims hereof.

[0079] Two fully-formulated 5W30 lubricating oil compositions (or lubricants) were blended by methods known in the art.

[0080] Each lubricant was formulated to have the same kinematic viscosity at 100°C and contained or possessed:

a calcium salicylate detergent additive, TBN 160, giving rise to 0.114 mass % of Ca atoms;
a phosphorus content of 0.05 mass %;
a polymer content of 0.9 mass %; and
identical quantities of dispersant, antiwear agent, antioxidant, friction modifier and other
additives, routinely used in formulating lubricating oil compositions.

[0081] The two lubricants differed in that:

Lubricant 1, a lubricant of the invention, contained as a viscosity index improver 6 mass % of an isoprene/styrene linear diblock copolymer in 130N Group I basestock with 1.9 mass % polymethacrylate LOFI. The copolymer, having one block derived from styrene and one block of hydrogenated polyisoprene, had a styrene content of 35 mass % and a number average molecular weight (measured as styrene equivalent) of 130,000; and

[0082] Lubricant A, a reference lubricant, contained as a viscosity index improver 15 mass % of star copolymer in 130N Group I basestock. The star copolymer had hydrogenated polyisoprene arms and an overall number average molecular weight (measured as styrene equivalent) of 360,000.

[0083] Each of the two lubricants was tested for cam and lifter wear according to the Sequence IIIG Test. The Test utilizes a 1996 General Motors 3800 cc Series II, water-cooled, 4 cycle, V-6 gasoline engine as the test apparatus. The Sequence III G test engine is an overhead valve design (OHV) and uses a single camshaft operating both intake and exhaust valves via pushrods and hydraulic valve lifters in a sliding-follower arrangement. Using unleaded gasoline, the engine runs a 10-minute initial oil-leveling procedure followed by a 15-minute slow ramp up to speed and load conditions. The engine then operates at 125 bhp, 3,600 rpm and 150° C oil temperature for 100 hours, interrupted at 20-hour intervals for oil level checks.

[0084] At the end of the Test, the cam lobes and lifters were measured for wear. The results, expressed as average cam-plus-lifter wear in microns, were as follows, where the pass limit for the Test is a maximum of 60 microns.

Lubricant 1 : 57.2

(continued)

Lubricant A : 291.7

5 **[0085]** The results demonstrate that the use of a linear diblock viscosity index improver in Lubricant 1 gave rise to dramatically better wear performance in an accredited engine test compared to Lubricant A.

Claims

- 10
1. An internal combustion engine crankcase lubricating oil composition having a phosphorus concentration, expressed as atoms of phosphorus, of not greater than 0.09 mass %, based on the mass of the oil composition, which composition comprises or is made by admixing:
 - 15 (A) an oil of lubricating viscosity, in a major amount;
 - (B) a metal detergent system, as an additive in a minor amount, comprising one or more metal salts of organic carboxylic acids; and
 - (C) a viscosity index improver comprising a linear diblock copolymer comprising at least one block derivable primarily from a vinyl aromatic hydrocarbon monomer and at least one block derivable primarily from a diene monomer.
 2. An oil composition as claimed in claim 1 wherein the linear diblock copolymer is at least one diblock copolymer comprising at least a polystyrene block and a block derived from isoprene, butadiene or a mixture thereof.
 - 25 3. An oil composition as claimed in claim 2 wherein the linear diblock copolymer is at least one diblock copolymer selected from the group consisting of hydrogenated styrene/butadiene diblock copolymers and hydrogenated styrene/isoprene diblock copolymers.
 4. An oil composition as claimed in claim 2 or claim 3 wherein the diblock copolymer has a Shear Stability Index value of from 2 to 50% (30 cycles) and the polydiene block of the diblock copolymer comprises from 40 to 90 mass % derived from isoprene and from 10 to 60 mass % derived from butadiene.
 - 30 5. An oil composition as claimed in any one of claims 1 to 4 wherein the diblock copolymer has a Shear Stability Index value of from 5 to 25% (30 cycles).
 - 35 6. An oil composition as claimed in any of claims 1 to 5 having a sulphated ash concentration of not greater than 1.0 mass %.
 7. An oil composition as claimed in any of claims 1 to 6 having a sulphur concentration, expressed as atoms of sulphur, of not greater than 0.3, preferably not greater than 0.2, mass %.
 - 40 8. An oil composition as claimed in any of claims 1 to 7 wherein the metal salts of organic carboxylic acids are overbased alkaline earth metal salicylates.
 9. An oil composition as claimed in any of claims 1 to 8 further including one or more additives, other than (B) and (C), selected from dispersants, detergents, antioxidants, antiwear agents, friction modifiers, corrosion inhibitors, pour point depressants, demulsifiers and anti-foaming agents.
 - 45 10. A method of lubricating a compression-ignited or spark-ignited internal combustion engine which comprises supplying to the engine a lubricating oil composition as claimed in any of claims 1 to 9.
 - 50 11. The use of a viscosity index improver as defined in any of claims 1 to 5 to improve the cam and lifter wear in the crankcase lubrication of an internal combustion engine by a lubricating oil composition having a phosphorus concentration, expressed as atoms of phosphorus, of not greater than 0.09 mass %, based on the mass of the lubricating oil composition and comprising a metal detergent system as defined in any of claims 1, 7 and 8.
 - 55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1338643 A [0005]
- US 5808145 A [0038]
- EP 0933417 A [0038]
- EP 0985726 A [0038]
- EP 0708171 A [0040]
- WO 990025677 A [0040]
- WO 020072529 A [0040]
- WO 030018728 A [0040]
- US 3113986 A [0049]
- US 3700633 A [0049] [0049]
- US 3634595 A [0049]
- US 3670054 A [0049]
- US RE27145 E [0049]
- US 5141996 A [0056]
- WO 9813443 A [0056]
- WO 9921902 A [0056]
- US 4146489 A [0056]
- US 4292414 A [0056]
- US 4506056 A [0056]
- US 4867890 A [0065]
- US 2719125 A [0068]
- US 2719126 A [0068]
- US 3087932 A [0068]
- US 3821236 A [0068]
- US 3904537 A [0068]
- US 4097387 A [0068]
- US 4107059 A [0068]
- US 4136043 A [0068]
- US 4188299 A [0068]
- US 4193882 A [0068]
- GB 1560830 A [0068]
- EP 330522 A [0069]
- US 4938880 A [0075]

Non-patent literature cited in the description

- *J. Polymer Science, Part A: Polymer Chemistry*, 1988, vol. 26, 1189-1198 [0056]
- *J. Polymer Science, Polymer Letters*, 1982, vol. 20, 481-486 [0056]
- **GAYLORD ; MEHTA.** *J. Polymer Science, Polymer Letters*, 1983, vol. 21, 23-30 [0056]
- Degradation and Crosslinking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides. *J. Applied Polymer Science*, 1987, vol. 33, 2549-2558 [0056]