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(57) Abstract

A lubricating oil composition comprises a major amount of an oil of lubricating viscosity and a minor amount of an additive combination comprising an ashless dispersant having a polymeric hydrocarbon backbone of $\overline{M}n$ between 1000 and 4000 and a dialkyl phosphorodithioic acid metal salt, in which of the alkyl groups, at least 70 mole % are secondary having 6 carbon atoms, no more than 15 mole % are primary, and no more than 15 mole % are secondary having less than 6 carbon atoms.

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LUBRICATING COMPOSITIONS

This invention relates to lubricating oils having improved wear properties, particularly oils for crankcase lubrication of gasoline and/or diesel engines.

Lubricating oils for use in gasoline and diesel crankcases require regular improvement in performance to meet the demands of spark-ignited and diesel engines which are continually being uprated. As the power output and complexity of engines increase the lubricating oils used in the engines need to have improved performance in respect of wear control and a reduction in the formation of undersirable deposits, such as varnish, sludge, carbonaceous and resinous materials which can form in the engines, adhering to the engine components and reducing the efficiency of the engine.

The problem of reducing engine deposits has been conventionally addressed by using a wide variety of ashless dispersants which are typically oil-soluble additives comprising long chain hydrocarbon polymers substituted with mono- or dicarboxylic acid producing moieties, preferably dicarboxylic acid or anhydride moieties. Polyisobutylene polymers having a number average molecular weight ($\overline{M}n$) of from 900 to 2500, substituted with succinic anhydride groups, have been extensively used as the basis for useful dispersants.

Other polymers, such as ethylene-propylene copolymers and terpolymers containing non-conjugated dienes, have been disclosed as suitable polymers for the preparation of ashless nitrogen and ester dispersants. US-A-4234435, for example, discloses dispersants prepared from polyalkenes of $\overline{M}n$ between 1300 and 5000. The polyalkene can comprise homopolymers or interpolymers of C2 to C16 terminal olefins, of which ethylene-propylene copolymers are given as examples, with specific reference to a copolymer of 80% ethylene and 20% propylene.

A new class of ashless dispersants comprising functionalised and/or derivatised olefin polymers, particularly ethylene/alpha-olefin polymers, has been produced using metallocene catalyst systems. Such dispersants are described in US-A-5128056, 5151204, 5200103, 5225092, 5266223, 5334775; WO-A-94/19436, 94/13709; and EP-A-440506, 513157 and 513211. These dispersants have improved viscometric properties as expressed in a ratio of CCS viscosity to kV 100°C. Useful dispersants of this type have a hydrocarbon polymer moiety with a $\overline{M}n$ of 700 to 5000, preferably 1600 to 3500.

These ashless dispersants are effective for reducing engine deposits and the concentration of ashless dispersant in the lubricating oils can be increased to meet the increase in intervals between oil changes required by motor manufacturers. However, at the higher levels of ashless dispersant required it has been observed that higher engine wear can occur, particularly when the engine is operating under low temperature conditions. This increase in wear is believed to arise from complex interactions between the ashless dispersants and other additives in the lubricating oil, particularly the metal salts of dihydrocarbyl phosphorodithioic acids, usually present in combination with the ashless dispersants.

Metal salts of dihydrocarbylphosphorodithioic acids are commonly used with ashless dispersants to achieve improved anti-wear and antioxidant properties. EP-A-379566 discloses a lubricating oil composition for internal combustion engines which comprises

(A) a major amount of oil of lubricating viscosity

(B) at least 2.0% by weight of at least one carboxylic derivative composition obtainable by reacting

  (B-1) at least one substituted succinic acylating agent with

  (B-2) at least one amine compound characterized by the presence within its structure of at least one HN< group wherein said substituted succinic acylating agents consist of substituent groups and succinic groups wherein the substituent groups are derived from polyalkene, said polyalkene being characterized by a $\overline{M}n$ value of 1300 to about 5000 and a $\overline{M}w/\overline{M}n$ value of about 1.5 to about 4.5, said acylating agents being characterized by the presence within their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups, and

(C) from about 0.05 to about 5% by weight of a mixture of metal salts of dihydrocarbyl phosphorodithioic acids wherein in at least one of the dihydrocarbyl phosphorodithioic acids, one of the hydrocarbyl groups (C-1) is an isopropyl or secondary butyl group, the other hydrocarbyl group (C-2) contains at least five carbon atoms, and at least about 20 mole percent of all of the hydrocarbyl groups present in (C) are isopropyl groups, secondary butyl groups or mixtures thereof, provided that at least about 25 mole percent of the hydrocarbyl groups in (C) are isopropyl groups, secondary butyl groups, or mixtures thereof when the lubrication oil compositions comprise less than about 2.5% by weight of (B);

provided that when the carboxylic derivative composition (B) is produced by reacting the acylating agent (B-1) with from about 0.70 equivalent up to less than one equivalent, per equivalent of acylating agent, of the amine compound (B-2), then at least about 20 mole % of all of the hydrocarbon groups present in (C) are secondary butyl groups or mixtures of isopropyl groups and secondary butyl groups.

The specification describes the preparation of a variety of dihydrocarbyl phosphorodithioic metal salts but contains no exemplification of compositions containing the additives by which to judge their effectiveness. The problem of the increased wear brought about using combinations of ashless dispersants and the phosphorodithioic metal salts is not disclosed.

WO 89/06237 discloses the preparation of basic metal dihydrocarbylphosphorodithioates and phosphoromonothioates by employing a catalytic amount of alkali or alkaline earth metal hydroxide or mixtures thereof. However, it does not address the problem of wear under low temperature conditions.

US-A-4529526 discloses a lubricating oil composition comprising:

a) oil;
b) sulfurised oxymetal organophosphorodithioate of a specific formula and/or sulfurised oxymetal dithiocarbamate of a specific formula;
c) at least one ZDDP of a specific formula;
d) calcium benzenesulfonate and/or calcium petroleumsulfonate; and
e) alkenylsuccinic acid imide and/or boron derivatives thereof.

Such a composition is described as providing superior reduction in mechanical friction loss of four-cycle engines. The dispersants specifically disclosed in the specification have polymers with number average molecular weight of less than 1000.

It has now been found that the problem of increased engine wear, particularly under low temperature conditions, can be reduced by using a metal salt of a dihydrocarbyl phosphorodithioic acid in the lubricating oil composition wherein the hydrocarbyl groups of the acid are certain hydrocarbyl groups containing selected number of carbon atoms in combination with an ashless dispersant comprising a polymer backbone having a selected number average molecular weight range.

SUMMARY OF INVENTION

According to the first aspect of the present invention there is provided a lubricating oil composition, such as for crankcase lubrication of gasoline or diesel engines, obtained by mixing:

(A) a major amount of an oil of lubricating viscosity,

(B) at least 0.00045 mole per 100 g of the total composition of an ashless dispersant comprising an oil soluble polymeric hydrocarbon backbone having functional groups in which the hydrocarbon backbone has a number average molecular weight of between 1000 and 4000, and

(C) from 0.0005 to 0.002 mole per 100 g of the total composition of at least one dihydrocarbyl phosphorodithioic acid metal salt wherein at least 70 mole % of the hydrocarbyl groups are secondary alkyl groups of 6 carbon atoms, no more than 15 mole % of the hydrocarbyl groups are primary alkyl groups, and no more than 15 mole % of the hydrocarbyl groups are secondary alkyl groups having less than 6 carbon atoms, and the metal of the salt being selected from alkali metal, alkaline earth metal, aluminum, iron, cobalt, bismuth, lead, tin, molybdenum, manganese, nickel, copper and zinc.

A second aspect of the present invention provides a lubricating oil concentrate comprising 3 to 60 weight percent of component (B) and 1 to 20 weight percent of component (C) in a base oil of lubricating viscosity, wherein components (B) and (C) are defined as in the first aspect.

A third aspect of the present invention provides the use in a lubricating oil composition of a dihydrocarbyl phosphorodithioic acid metal salt according to component (C) defined in the first aspect for improving the wear protection of spark-ignited and diesel engines under low temperature conditions.

A fourth aspect of the present invention provides the use in spark-ignited or diesel engines of a lubricating oil composition as defined in the first aspect for improving the wear protection of said spark-ignited or diesel engines.

The features of the invention will now be discussed in further detail as follows.

Component (A): oil of lubricating viscosity

The oil of lubricating viscosity 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 centistokes to 30 centistokes, especially 5 centistokes to 20 centistokes, at 100°C as measured by ASTM D445.

Natural oils include animal oils and vegetable oils (e.g., castor, lard oil) liquid petroleum oils and hydrorefined, solvent-treated or acid-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.

Synthetic lubricating oils include hydrocarbon oils and halo-substituted 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); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives; analogs and homologs thereof. Also suitable are poly alpha-olefin synthetic oils.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C3-C8 fatty acid esters and C13 Oxo acid diester of tetraethylene glycol.

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, subericacid, 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, di-isooctyl azelate, di-isodecyl 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.

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.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl)silicate, hexa-(4-methyl-2-pentoxy)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined 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 an 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. Rerefined 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 rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

Component (B): ashless dispersants

Preferably at least 0.0006 mole, of ashless dispersant, per 100 g of the total composition may be used in the present invention, more preferably at least 0.00061, especially at least 0.00062 mole per 100 g of the total composition. The oil compositions of the present invention use at most 0.0014 mole, of ashless dispersant, per 100 g of the total composition, preferably at most 0.0013, such as at most 0.0012 mole per 100 g of the total composition. For example, depending on the molecular weight of the ashless dispersant as described herein below, the ashless dispersant may be employed in an amount of at least

1.92, more preferably at least 2.56, most preferably at least 2.60, advantageously at least 2.65 % by weight based on the weight of the total composition; and at most 6.00, preferably at most 5.50, such as at most 5.10 % by weight based on the weight of the total composition.

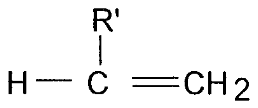
The high molecular weight ashless dispersants of the composition of the invention include the range of ashless dispersants known as effective for adding to lubricant oils for the purpose of reducing the formation of deposits in gasoline or diesel engines. A wide variety of such compounds is available, as now described in more detail.

The ashless dispersant comprises 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 dispersant 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 polyalkylene polyamine.

Processes for reacting polymeric hydrocarbons with unsaturated carboxylic acids, anhydrides or esters and the preparation of derivatives from those compounds are disclosed in US-A-3087936, US-A-3172892, US-A-3215707, US-A-3231587, US-A-3231587, US-A-3272746, US-A-3275554, US-A-3381022, US-A-3442808, US-A-356804, US-A-3912764, US-A-4110349, US-A-4234435 and GB-A-1440219.

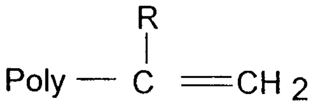
A class of ashless dispersants comprising ethylene alpha-olefin copolymers and alpha-olefin homo- and copolymers prepared using new metallocene catalyst chemistry, which may have a high degree (e.g. >30%) of terminal vinylidene unsaturation is described in US-A-5128056, 5151204, 5200103, 5225092, 5266223, 5334775; WO-A-94/19436, 94/13709; and EP-A-440506, 513157, 513211. These dispersants are described as having superior viscometric properties as expressed in a ratio of CCS viscosity to kV 100°C.

The term "alpha-olefin" is used herein to denote an olefin of the formula



$$\mathrm{H}-\overset{\mathrm{R'}}{\overset{|}{\mathrm{C}}}=\mathrm{CH_2}$$

wherein R' is preferably a C1-C18 alkyl group. The requirement for terminal vinylidene unsaturation refers to the presence in the polymer of the following structure:



$$\mathrm{Poly}-\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}=\mathrm{CH_2}$$

wherein Poly is the polymer chain and R is typically a C1-C18 alkyl group, typically methyl or ethyl. Preferably the polymers will have at least 50%, and most preferably at least 60%, of the polymer chains with terminal vinylidene unsaturation. As indicated in WO-A-94/19436, ethylene/1-butene copolymers typically have vinyl groups terminating no more than about 10 percent of the chains, and internal mono-unsaturation in the balance of the chains. The nature of the unsaturation may be determined by FTIR spectroscopic analysis, titration or C-13 NMR.

The oil-soluble polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene) or a copolymer of two or more of such olefins: for example, copolymers of ethylene and an alpha-olefin such as an alpha-olefin containing up to 8, preferably up to 6, such as up to 4 carbon atoms (e.g. propylene, butylene, hexene or octene), or copolymers of two different alpha-olefins. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is an α,ω-diene, such as a C3 to C22 non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene).

Atactic propylene oligomers typically having a $\overline{M}_n$ of from 1000 to 4000 may also be used, as described in EP-A-490454, as well as heteropolymers such as polyepoxides.

One preferred class of olefin polymers is polybutenes and specifically poly-n-butenes, such as may be prepared by polymerization of a C4 refinery stream. Other preferred classes of olefin polymers are EAO copolymers that preferably contain 1 to 50 mole % ethylene, and more preferably 5 to 48 mole % ethylene. Such polymers may contain more than one alpha-olefin and may contain one or more C3 to C22 diolefins. Also usable are mixtures of EAO's of varying ethylene content. Different polymer types, e.g., EAO, may also be mixed or blended, as well as polymers differing in $\overline{M}_n$; components derived from these also may be mixed or blended.

The olefin polymers and copolymers used in the dispersant employed in the invention preferably have an $\overline{M}_n$ of from 1000 to 4000, more preferably at least 1100, advantageously at least 1200, for example 1300 to 4000, especially 1600 to 4000, such as from 2000 to 4000. Polymer molecular weight, specifically $\overline{M}_n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

The degree of polymerisation Dp of a polymer is:

$$D_p = \sum_i \frac{\text{Mn x mol.\% monomer i}}{\text{100 x mol.wt monomer i}}$$

and thus for the copolymers of two monomers Dp may be calculated as follows:

$$D_p = \frac{\text{Mn x mol.\% monomer 1}}{\text{100 x mol.wt monomer 1}} + \frac{\text{Mn x mol.\% monomer 2}}{\text{100 x mol.wt monomer 2}}$$

Preferably, the degree of polymerisation for the polymer backbones used in the invention is at least 45, typically from 50 to 165, more preferably 55 to 140.

Particularly preferred copolymers are ethylene butene copolymers.

Preferably, the olefin polymers and copolymers may be prepared by various catalytic polymerization processes using metallocene catalysts which are, for example, bulky ligand transition metal compounds of the formula:

[L]mM[A]n

where L is a bulky ligand; A is a leaving group, M is a transition metal, and m and n are such that the total ligand valency corresponds to the transition metal valency. Preferably the catalyst is four co-ordinate such that the compound is ionizable to a 1^+ valency state.

The ligands L and A may be bridged to each other, and if two ligands A and/or L are present, they may be bridged. The metallocene compound may be a full sandwich compound having two or more ligands L which may be cyclopentadienyl ligands or cyclopentadienyl derived ligands, or they may be half sandwich compounds having one such ligand L. The ligand may be mono- or polynuclear or any other ligand capable of η-5 bonding to the transition metal.

One or more of the ligands may π-bond to the transition metal atom, which may be a Group 4, 5 or 6 transition metal and/or a lanthanide or actinide transition metal, with zirconium, titanium and hafnium being particularly preferred.

The ligands may be substituted or unsubstituted, and mono-, di-, tri, tetra- and penta-substitution of the cyclopentadienyl ring is possible. Optionally the substituent(s) may act as one or more bridges between the ligands and/or leaving groups and/or transition metal. Such bridges typically comprise one or more of a carbon, germanium, silicon, phosphorus or nitrogen atom-containing radical, and preferably the bridge places a one-atom link between the entities being bridged, although that atom may and often does carry other substituents.

The metallocene may also contain a further displaceable ligand, preferably displaced by a cocatalyst - a leaving group - that is usually selected from a wide variety of hydrocarbyl groups and halogens.

Such polymerizations, catalysts, and cocatalysts or activators are described, for example, in US-A-4530914, 4665208, 4808561, 4871705, 4897455, 4937299, 4952716, 5017714, 5055438, 5057475, 5064802, 5096867, 5120867, 5124418, 5153157, 5198401, 5227440, 5241025; EP-A-129368, 277003, 277004, 420436, 520732; and WO-A-91/04257, 92/00333, 93/08199, 93/08221, 94/07928 and 94/13715.

The oil-soluble polymeric hydrocarbon backbone may be functionalized to incorporate a functional group into the backbone of the polymer, or as one or more groups pendant from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, halogen, or boron. It can be attached to a saturated hydrocarbon part of the oil-soluble polymeric hydrocarbon backbone via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer in conjunction with oxidation or cleavage of the polymer chain end (e.g., as in ozonolysis).

Useful functionalization reactions include: halogenation of the polymer at an olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound (e.g., maleation where the polymer is reacted with maleic acid or anhydride); reaction of the polymer with an unsaturated functional compound by the "ene" reaction absent halogenation; reaction of the polymer with at least one phenol group (this permits derivatization in a Mannich base-type condensation); reaction of the polymer at a point of unsaturation with carbon monoxide using a Koch-type reaction to introduce a carbonyl group in an iso or neo position; reaction of the polymer with the functionalizing compound by free radical addition using a free radical catalyst; reaction with a thiocarboxylic acid derivative; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination, or ozonolysis.

The functionalized oil-soluble polymeric hydrocarbon backbone is then further derivatized with a nucleophilic reactant such as an amine, amino-alcohol, alcohol, metal compound or mixture thereof to form a corresponding derivative. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Particularly useful amine compounds include mono- and polyamines, e.g. polyalkylene and polyoxyalkylene polyamines of about 2 to 60, conveniently 2 to 40 (e.g., 3 to 20), total carbon atoms and about 1 to 12, conveniently 3 to 12, and preferably 3 to 9 nitrogen atoms in the molecule. Mixtures of amine compounds may advantageously be used such as those prepared by reaction of alkylene dihalide with ammonia. Preferred amines are aliphatic saturated amines, including, e.g., 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines. A particularly useful class of amines are the polyamido and related amido-amines as disclosed in US 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (THAM) as described in US 4,102,798; 4,113,639; 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structure amines may also be used. Similarly, one may use the condensed amines disclosed in US 5,053,152. The functionalized polymer is reacted with the amine compound according to conventional techniques as described in EP-A-208,560; US 4,234,435 and US 5,229,022 .

The functionalized oil-soluble polymeric hydrocarbon backbones also may be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols or with aromatic compounds such as phenols and naphthols. Polyhydric alcohols are preferred, e.g., alkylene glycols in which the alkylene radical contains from 2 to 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof. An ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding ashless dispersants comprise the ether-alcohols and including, for example, the oxy-alkylene, oxy-arylene. They are exemplified by ether-alcohols having up to 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms. The ester dispersants may be di-esters of succinic acids or acidic esters, i.e., partially esterified succinic acids, as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxyl radicals. An ester dispersant may be prepared by one of several known methods as illustrated, for example, in US 3,381,022.

A preferred group of ashless dispersants includes those substituted with succinic anhydride groups and reacted with polyethylene amines (e.g., tetraethylene pentamine), aminoalcohols such as trismethylolaminomethane and optionally additional reactants such as alcohols and reactive metals e.g., pentaerythritol, and combinations thereof). Also useful are dispersants wherein a polyamine is attached directly to the backbone by the methods shown in US 3,275,554 and 3,565,804 where a halogen group on a halogenated hydrocarbon is displaced with various alkylene polyamines.

Another class of ashless dispersants comprises Mannich base condensation products. Generally, these are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compounds (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles polyalkylene polyamine as disclosed, for example, in US 3,442,808. Such Mannich condensation products may include a polymer product of a metallocene cataylsed polymerisation as a substituent on the benzene group or may be reacted with a compound containing such a polymer substituted on a succinic anhydride, in a manner similar to that shown in US 3,442,808.

Examples of functionalized and/or derivatized olefin polymers based on polymers synthesized using metallocene catalyst systems are described in publications identified above.

The dispersant can be further post-treated by a variety of conventional post treatments such as boration, as generally taught in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from the group consisting of boron oxide, boron halides, boron acids and esters of boron acids, in an amount to provide from about 0.1 atomic proportion of boron for each mole of the acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of the acylated nitrogen composition. Usefully the dispersants contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of the borated acyl nitrogen compound. The boron, which appears be in the product as dehydrated boric acid polymers (primarily (HBO2)3), is believed to attach to the dispersant imides and diimides as amine salts e.g., the metaborate salt of the diimide. Boration is readily carried out by adding from about 0.05 to 4, e.g., 1 to 3 wt. % (based on the weight of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135° to 190° C, e.g., 140°-170° C, for from 1 to 5 hours followed by nitrogen stripping. Alternatively, the boron treatment can be carried out by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine while removing water.

As previously indicated, the use of increased levels of ashless dispersants in lubricating compositions to achieve longer intervals between oil changes in an engine has been observed to result in increased engine wear. It is believed that this occurs because the dihydrocarbyl phosphorodithioic acid salts used as the antiwear component of the lubricating oil becomes less effective with increasing concentration of ashless dispersant. This reduction in effectiveness is believed to result from association of the ashless dispersant with the antiwear agent so that it is less available for conferring antiwear properties on the engine parts. The reduction in the effectiveness of the antiwear agents appears to be greatest for those ashless dispersants which are most effective at reducing engine deposits. Thus, the dispersants which are most effective at associating with and suspending foreign particles in the engine oil are also observed to reduce the effectiveness of the antiwear agents to the greatest extent, and exert their deleterious effect at lower concentrations of ashless dispersant than less effective ashless dispersants. Thus the invention is particularly useful for providing improved wear to those lubricating compositions containing ashless dispersants which are most effective in reducing engine deposits.

Particularly useful compositions of the invention are those containing ashless dispersants based on poly(isobutylene) polymers having a number average molecular weight of from 1300 to 2500, preferably 1600 to 2500, more preferably 2000 to 2500, substituted with succinic anhydride groups which have been further functionalised. Preferably, the dispersant contains at least 1.0, and desirably at least 1.3 succinic groups per polymer group. A preferred functionalising class of compounds contains at least one NH< group. Generally, functionalisation is effected using from 0.5 equivalents to 2 moles of amine compound per equivalent of succinic anhydride substituted polymer.

Other preferred ashless dispersants are the functionalised and derivatised olefin polymers based on ethylene alpha-olefin polymers previously described, produced using metallocene catalyst systems. These, preferably, have number average molecular weights of from 1600 to 3500, more preferably 2000 to 3500, especially 2500 to 3500.

For the avoidance of doubt, ashless dispersants comprising a polymeric hydrocarbon backbone having number average molecular weight less than 1000 may also be used in combination with ashless dispersants of the invention.

Component (C): metal salt

Preferably component (C) may be used in the present invention in a range of from 0.00055 to 0.0019 mole per 100 g of the total composition, more preferably from 0.0006 to 0.00185, especially from 0.0007 to 0.0017 mole per 100 g of the total composition. For example, depending on the molecular weight of the metal salt as described herein below, the metal salt may be used in a range of from 0.330 to 1.320, preferably from 0.363 to

1.255, more preferably from 0.396 to 1.221, most preferably from 0.462 to 1.122 % by weight based on the weight of the total composition.

As used herein, the term "hydrocarbyl" denotes a radical having a carbon atoms directly attached to the remainder of the molecule and having predominatly hydrocarbon character within the context of this invention. Such radicals include the following:

(1) Hydrocarbon radicals; that is, aliphatic, e.g. alkyl or alkenyl, alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicylic radicals, as well as cyclic radicals wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicylic radical).

(2) Substituted hydrocarbon radicals; that is, radicals containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the radical. Those skilled in the art will be aware of suitable substituents; examples are halo (particularly chloro and fluoro), alkoxy, mercapto, nitro, nitroso, sulfoxy, and other groups.

(3) Hetero radicals; that is, radicals which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen, and sulfur.

Preferably, the hydrocarbyl groups are alkyl groups and may be linear or branched; preferred are branched alkyl groups.

The metal salt component may be a mixture of salts provided that the dialkyl content of the mixture of salts conforms to the limits set out above.

In the most preferred form of the dialkyl salt 100 mole % of the dialkyl groups are secondary alkyl groups containing 6 carbon atoms, i.e. if a single metal salt is used both alkyl groups of the compound, denoted by R1 and R2, are secondary C6 alkyl groups. The minimum molar percentage of secondary C6 alkyl groups in component (C) is 70 mole %, i.e. at least 70 mole % of the total of R1 and R2 are secondary C6 alkyl groups, preferably at least 80, more preferably at least 90 mole %. The remainder of the alkyl groups in the compound, if any, are selected from primary groups, secondary groups having less than 6 carbon atoms and secondary groups having more than 6 carbon atoms, provided that there are present no more than 15, preferably no more than 10, especially no more than 5 mole % of either primary groups or secondary groups containing less than 6 carbon atoms. These considerations apply whether component (C) is present as a single compound or a mixture of compounds. Thus, component (C) may be a mixture of a salt of a dihydrocarbyl phosphorodithoic acid in which 100 mole % of the alkyl groups are secondary C6 groups, in admixture with other dialkyl phosphorodithoic acid salts provided that the total alkyl group concentrations of the mixture fall within the prescribed limits.

A preferred secondary C6 alkyl group is 4-methyl-2-pentyl. Other suitable secondary C6 groups include the isomers of methyl-pentyl, dimethyl butyl and ethyl butyl, for example 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl and 3-methyl-2-pentyl.

The primary groups may include isobutyl, n-butyl, n-amyl, n-hexyl, n-heptyl, 2-ethylhexyl, iso-octyl, nonyl and higher alkyl groups.

The secondary groups containing less than 6 carbon atoms include sec-butyl. Secondary groups containing more than 6 carbon atoms preferably contain no more than 10 carbon atoms.

The preferred metal salt of the dihydrocarbyl phosphordithoic acid is zinc, for example those represented by the formula $Zn[SP(S)(OR^1)(OR^2)]_2$, where R^1 and R^2 are defined as above.

They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound.

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 neutralization reaction.

Neutral, or normal, and basic metal salts of dihydrocarbyl phosphordithioic acids can be employed within the present invention. By "basic" it is meant those salts that have a higher ratio of equivalents of total metal to equivalents of the dihydrocarbyl phosphordithioic acid than that of the corresponding "neutral" or "normal" salt. Neutral, or normal, metal salts have one equivalent of metal per one equivalent of the dihydrocarbyl phosphordithioic acid.

Components (B) and (C) must be "oil-soluble" or "oil-dispersible" in the oil of lubricating viscosity, but these do not mean that they are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. They do mean, however, that (B) and (C) are, for instance, soluble or stably dispersible in the oil to an extent sufficient to exert their intended effect in the environment in which the lubricating oil composition is employed. Moreover, the additional incorporation of other additives such as those described hereinafter may affect the oil-solubility or dispersibility of one or both of (B) and (C).

It should be appreciated that interaction may take place between the additive components of the invention after they have been mixed in the lubricating oil, in either the process of mixing or any subsequent condition to which the composition is exposed, including the use of the composition in its working environment. Interactions may also take place when further auxiliary additives are added to the compositions of the invention. Such interaction may include interaction which alters the chemical constitution of the additive. Thus, the compositions of the invention include compositions in which interaction between any of the additive components has occurred, as well as compositions in which no interaction has occurred between the components mixed in the lubricating oil.

Components (B) and (C) may be mixed with the oil of lubricating viscosity (component (A)) in any convenient way. For example, each of (B) and (C) can be added directly to the oil by dispersing or dissolving in the oil at the desired level of concentration at ambient or elevated temperature. They may be added individually or together to the oil.

Where added together, they are conveniently added in the form of concentrate in an oleaginous carrier.

Oil concentrate

Example of suitable oleaginous carriers are oils of lubricating viscosity, such as those described in detail hereinbefore, and aliphatic, naphthenic and aromatic hydrocarbons.

In such concentrates, there may be present from 1 to 90% by weight of the total weight of concentrate a mixture of components (B) and (C), preferably from 10 to 90% by weight, more preferably from 20 to 85% by weight. Preferably, the ashless dispersant (B) is present in an amount of from 3 to 60% by weight of the concentrate, more preferably from 20 to 60 % by weight, most preferably from 30 to 60 % by weight of the concentrate. The dihydrocarbyl phosphorodithioic acid metal salt (C) is preferably present in an amount of from 1 to 20% by weight of the concentrate, more preferably from 3 to 19 % by weight, most preferably from 5 to 17 % by weight of the concentrate. One or more additional additives, such as described hereinafter, may also be present in such concentrates.

OTHER ADDITIVE COMPONENTS

As indicated above, additional additives may be incorporated in the compositions of the invention to enable them to meet particular requirements. Examples of additives which may be included in the lubricating oil compositions are detergents and metal rust inhibitors, viscosity index improvers, corrosion inhibitors, other oxidation inhibitors, friction modifiers, other dispersants, anti-foaming agents, anti-wear agents, pour point depressants, and rust inhibitors. Some are discussed in further detail below.

Detergents and metal rust inhibitors include, for example, the oil-soluble sulphonates, phenates, sulphurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals or magnesium, for example, sodium, lithium, calcium, barium and magnesium. The most commonly used metals are calcium and magnesium, mixtures of calcium and magnesium, and mixtures of calcium and/or magnesium with sodium. The detergents may be overbased: overbased detergents function both as detergents and acid neutralizers, thereby reducing wear and corrosion and extending engine life.

Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

Examples of supplementary antioxidants include, for example, aromatic amines, for example alkylated phenylamines and phenyl α-naphthylamine; hindered phenols; alkaline earth metal salts of sulphurized alkyl-phenols having preferably C5 to C12 alkyl side chains, e.g., calcium nonylphenyl sulphide; barium octylphenyl sulphide; hindered phenols; phosphosulphurized or sulphurized hydrocarbons; and oil-soluble copper compounds.

Friction modifiers and fuel economy agents which are compatible with the other ingredients of the final oil may also be included. Examples of such materials are molybdenum compounds and 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 alkoxylated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

A viscosity index improver dispersant functions both as a viscosity index improver and as a dispersant. Examples of viscosity index improver dispersants include reaction products of amines, for example polyamines, with a hydrocarbyl-substituted mono- or dicarboxylic acid in which the hydrocarbyl substituent comprises a chain of sufficient length to impart viscosity index improving properties to the compounds. In general, the viscosity index improver dispersant may be, for example, a polymer of a C4 to C24 unsaturated ester of vinyl alcohol or a C3 to C10 unsaturated mono-carboxylic acid or a C4 to C10 di-carboxylic acid with an unsaturated nitrogen-containing monomer having 4 to 20 carbon atoms; a polymer of a C2 to C20 olefin with an unsaturated C3 to C10 mono- or di-carboxylic acid neutralised with an amine, hydroxyamine or an alcohol; or a polymer of ethylene with a C3 to C20 olefin further reacted either by grafting a C4 to C20 unsaturated nitrogen - containing monomer thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting carboxylic acid groups of the grafted acid with an amine, hydroxy amine or alcohol.

Examples of dispersants and viscosity index improver dispersants may be found in European Patent Specification No. 24146 B.

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, and polymethacrylates. Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount which enables the additive to provide its desired function.

As indicated earlier, when a plurality of additives are employed it may be desirable, although not essential, to prepare one or more additive concentrates comprising the additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition.

The final composition may employ typically about 10 wt % of the additive-package, the remainder being oil of lubricating viscosity.

All weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, or upon the total weight of any additive-package or concentrate or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent in each additive.

EXAMPLES

This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted and which include preferred embodiments of the invention.

The wear properties of the compositions of the invention are evaluated in the following Example using the SMIRA Valve Train Wear Rig test, the results being expressed as wear scar, diameter, measured in µm. The SMIRA test is described in a publication by C.H. Bovington and A. Hubbard, entitled "Friction and Wear in the Internal Combustion Engine", I. Mech. E., London, 1989. This describes a motored single cam and follower arrangement in which load speed and temperature can be varied. The impact on wear is assessed by the difference in the size of the HV 30 mark before and after the test. The tests are performed under 3 sets of conditions: low speed at 40°C, high speed at 65°C and high speed at 120°C: the larger the wear scar, the poorer the effectiveness of the additive for wear control. The most significant of these results in the context of the present invention is the performance at low speed at 40°C.

The Example shows the results of a statistically designed experiment evaluating the effect of variations of different zinc salts of various dialkyl phosphorodithioic acids in combination with various ashless dispersants, overbased and neutral metal detergents and antioxidants. These are typically present as components in lubricating oil compositions. It is necessary to evaluate the results on the basis of the statistical significance of the results because there are complex interactions between the various components of the compositions which are difficult to separate and interpret unless such a mathematical approach is adopted.

Example

A series of compositions containing the components shown in Table 1 were made up in a base lubricating oil according to the following procedure. The weights indicated in Table 1 are those of the additive, that is the active ingredient of the additive plus the diluent or oil.

A batch of base oil containing a viscosity modifier was made up by blending 6.2 parts by weight of an ethylene/propylene copolymer in a mixture of solvent refined 100 neutral and 150 neutral oil of American manufacture (87.6 parts by weight 100N to 6.2 parts by weight 150N). The molecular weight of the viscosity modifier had a range such that it had a Shear Stability Index as measured by CEC-L-14-A-88 of 88% (SSI = (Fresh Oil Viscosity - Used Oil Viscosity) / (Fresh Oil Viscosity - Base Oil Blend Viscosity)*100). The mixture of oil and viscosity modifier was stirred at 70°C for 1 hr. Each of the compositions listed in Table 1 were made up using aliquot portions of this base oil mixture. The blending of the listed ingredients was effected by adding the dispersant to a portion of the oil mixture and maintaining the mixture at 80°C for 2 hours. After cooling to 60°C the overbased and neutral detergents, zinc salt and antioxidant were added and the blend was maintained at 60°C for 1 hr.

The components indicated in Table 1 are identified as follows:

Dispersant 1	A dispersant having an ethylene/butene copolymer backbone of number average molecular weight = 3400, functionalised by the introduction of a carbonyl group by the Koch reaction and reacted in turn with a polyamine. The preparation of such dispersant is described in WO-A-94/13709.
Dispersant 2	A conventional polyisobutenyl succinimide having a polymer backbone of number average molecular weight = 2225.
Dispersant 3	As Dispersant 2 but having a number average molecular weight of 950 (PIB chain).
Overbased Detergent 1	A magnesium benzene sulphonate of total base number (TBN) = 400.

Overbased Detergent 2	A calcium benzene sulphonate of TBN = 300.
Overbased Detergent 3	A calcium benzene sulphonate of TBN = 400.
Overbased Detergent 4	A calcium phenate of TBN = 250.
Neutral Detergent 1	A calcium benzene sulphonate of TBN = 25.
Neutral Detergent 2	A calcium phenate of TBN = 155.
Neutral Detergent 3	A calcium salicylate of TBN = 64
DDP 1	A zinc salt of a dialkyl phosphorodithioic acid containing 58 mole % of secondary C6 groups and 42 mole % of isopropyl groups.
DDP 2	As DDP 1, but containing 100 mole % of 4-methyl-2-pentyl groups. DDP 2 is an example of a metal salt of the present invention.
DDP 3	As DDP 1, but containing 77 mole % of isobutyl groups and 23 mole % of iso-amyl groups.
DDP 4	As DDP 1, but containing 100 mole % of iso-octyl groups.
Antioxidant 1	A copper salt of polyisobutenyl succinimide.
Antioxidant 2	Nonyl phenol sulpide.
Antioxidant 3	A hindered phenol.
Antioxidant 4	A diphenylamine antioxidant.

The results are shown in Table 2. Analysis of these results is shown in Tables 3 and 4. Table 3 shows the contribution the dispersant and the ZDDP confers to the measured wear property. The zinc salts provide the largest contribution (30.1%) under the low speed and low temperature condition; it is almost three times the unexplained variation in the experiment and is statistically significant at the 93% confidence interval. At high temperature, the zinc salts are less important, the dispersant having a larger impact.

It is seen from Table 4 that for the test where zinc salts have the predominant effect on the wear (i.e. the low speed test at 40°C) the zinc salt (2) conforming to the present invention has the best performance (the lowest wear, 3.61 μm) compared to the zinc salts (1), (2) and (3). Further, under the low speed and low temperature condition, the dispersant combination (1:3) of high and low number average molecular weight for the polymer (dispersant 1 with polymer $\overline{M}_n$ of 3400 and dispersant 3 with polymer $\overline{M}_n$ of 950) gave poor wear control indicating the preference for ashless dispersants comprising a polymer backbone with a selected number average molecular weight range.

TABLE 1

ADDITIVE FORMULATIONS, parts by weight

Experiment Number	Dispersant			Overbased Detergent				Neutral Detergent			DDP				Antioxidant			
	1	2	3	1	2	3	4	1	2	3	1	2	3	4	1	2	3	4
1	5			1.2				1.5			1.2				0.6			
2	5				1.65				1.5			1.2				1.2		
3	5					1.2				1.5			1.2				1.2	
4	5						2							1.2				1.2
5		6		1.2					1.5				1.2					1.2
6		6			1.65			1.5						1.2			1.2	
7		6				1.2					1.2					1.2		
8		6					2			1.5		1.2			0.6			
9	2.5	3		1.2						1.5				1.2		1.2		
10	2.5	3			1.65								1.2		0.6			
11	2.5	3				1.2		1.5				1.2						1.2
12	2.5	3					2		1.5		1.2						1.2	
13	2.5		3	1.2								1.2					1.2	
14	2.5		3		1.65					1.5	1.2							1.2
15	2.5		3			1.2			1.5					1.2	0.6			
16	2.5		3				2	1.5					1.2			1.2		
17	2.5	3		1.2						1.5		1.2						1.2
18	2.5	3			1.65						1.2						1.2	
19	2.5	3				1.2		1.5						1.2		1.2		
20	2.5	3					2		1.5				1.2		0.6			
21	2.5		3	1.2										1.2	0.6			
22	2.5		3		1.65					1.5			1.2			1.2		
23	2.5		3			1.2			1.5			1.2					1.2	
24	2.5		3				2	1.5			1.2							1.2
25	5			1.2				1.5					1.2				1.2	
26	5				1.65				1.5					1.2				1.2
27	5					1.2				1.5	1.2				0.6			
28	5						2					1.2				1.2		
29		6		1.2					1.5		1.2					1.2		
30		6			1.65			1.5				1.2			0.6			
31		6				1.2							1.2					1.2
32		6					2			1.5				1.2			1.2	

TABLE 2

VALVE TRAIN WEAR RIG RESULTS

Experiment Number	Dispersant	Overbased Detergent	Neutral Detergent	ZDDP	Anti-Ox	Test Results, (µm)		
						Low Speed @ 40°C	High Speed @ 65°C	High Speed @ 120°C
						7.428	10.428	16.714
1	1 (5 parts)	1	1	1	1	5.428	8.714	7.428
2	1 (5 parts)	2	2	2	2	5.857	5.428	10.714
3	1 (5 parts)	3	3	3	3	4.142	7.428	5
4	1 (5 parts)	4	None	4	4			
5	2 (6 parts)	1	2	3	4	6.571	8.428	10.142
6	2 (6 parts)	2	1	4	3	3.571	3	18.428
7	2 (6 parts)	3	None	1	2	4	4.857	11.571
8	2 (6 parts)	4	3	2	1	2.285	3.571	5.857
9	1:2 (2.5:3 parts)	1	3	4	2	3.571	7.428	9.857
10	1:2 (2.5:3 parts)	2	None	3	1	6.428	6.142	scuffed
11	1:2 (2.5:3 parts)	3	1	2	4	3.857	3.142	5.142
12	1:2 (2.5:3 parts)	4	2	1	3	6	6.285	12.71
13	1:3 (2.5:3 parts)	1	None	2	3	5	5	7.142
14	1:3 (2.5:3 parts)	2	3	1	4	3.142	3.285	5.714
15	1:3 (2.5:3 parts)	3	2	4	1	9.714	3.142	3.285
16	1:3 (2.5:3 parts)	4	1	3	2	6.285	2.714	6
17	1:2 (2.5:3 parts)	1	3	2	4	3.571	2.571	23.142
18	1:2 (2.5:3 parts)	2	None	1	3	3.714	2.571	5.857
19	1:2 (2.5:3 parts)	3	1	4	2	8.714	9.857	7.428
20	1:2 (2.5:3 parts)	4	2	3	1	3.428	4.571	7.142
21	1:3 (2.5:3 parts)	1	None	4	1	5.142	4	16.142
22	1:3 (2.5:3 parts)	2	3	3	2	6.428	5.428	4.714
23	1:3 (2.5:3 parts)	3	2	2	3	4.857	4	6.857
24	1:3 (2.5:3 parts)	4	1	1	4	4.571	5.142	5.428
25	1 (5 parts)	1	1	3	3	6	5.857	5.285
26	1 (5 parts)	2	2	4	4	4.285	7.571	6.571
27	1 (5 parts)	3	3	1	1	4.428	2.285	5
28	1 (5 parts)	4	None	2	2	2.571	2.714	5.428
29	2 (6 parts)	1	2	1	2	5.714	4	12.857
30	2 (6 parts)	2	1	2	1	1.285	2	18.428
31	2 (6 parts)	3	None	3	4	4	2.857	9.428
32	2 (6 parts)	4	3	4	3	4.857	3.285	5

TABLE 3

ANALYSIS OF VARIANCE

	40°C Low Speed		65°C High Speed		120°C High Speed	
	Confidence of an Effect	% Variation	Confidence of an Effect	% Variation	Confidence of an Effect	% Variation
Dispersant	74%	15.5%	80%	30.9	79%	26.2%
ZDDP	93%	30.1%	47%	13.8%	7%	2.2%
Interaction		10.6%		18.0%		15.5%
	TOTAL	100.0%		100.0%		100.0%

TABLE 4

AVERAGE WEAR FOR EACH COMPONENT

Component	SMIRA VTW Wear (µm)		
	40°C Low Speed	65°C High Speed	120°C High Speed
Dispersants			
1	5.02	6.30	7.77
1:2 (2.5:3)	4.91	5.32	13.28
1:3 (2.5:3)	5.64	4.09	6.91
2	4.04	4.00	11.46
DDP's			
1	4.87	4.86	9.48
3	5.62	5.18	11.05
4	5.50	5.71	8.96
2	3.61	3.96	9.93

CLAIMS

1. A lubricating oil composition, such as for crankcase lubrication of gasoline or diesel engines, obtained by mixing:
   (A) a major amount of an oil of lubricating viscosity,
   (B) at least 0.00045 mole per 100 g of the total composition of an ashless dispersant comprising an oil soluble polymeric hydrocarbon backbone having functional groups in which the hydrocarbon backbone has a number average molecular weight of between 1000 and 4000, and
   (C) from 0.0005 to 0.002 mole per 100 g of the total composition of at least one dihydrocarbyl phosphorodithioic acid metal salt wherein at least 70 mole % of the hydrocarbyl groups are secondary alkyl groups of 6 carbon atoms, no more than 15 mole % of the hydrocarbyl groups are primary alkyl groups, and no more than 15 mole % of the hydrocarbyl groups are secondary alkyl groups having less than 6 carbon atoms, and the metal of the salt being selected from alkali metal, alkaline earth metal, aluminum, iron, cobalt, bismuth, lead, tin, molybdenum, manganese, nickel, copper and zinc.

2. The oil composition according to claim 1 wherein the lubricating oil composition is for crankcase lubrication of gasoline and diesel engines.

3. The oil composition according to either claim 1 or claim 2 wherein the hydrocarbon backbone of component (B) has a number average molecular weight of between 1300 and 4000.

4. The oil composition according to any of claims 1 to 3 wherein the hydrocarbyl groups of component (C) are alkyl groups, at least 70 mole % of which are secondary alkyl groups of 6 carbon atoms, no more than 15 mole % are primary alkyl groups, and no more than 15 mole % are secondary alkyl groups having less than 6 carbon atoms.

5. The oil composition according to any of the preceding claims wherein the hydrocarbyl groups of component (C) consist wholly of secondary alkyl groups containing 6 carbon atoms.

6. The oil composition according to any of the preceding claims wherein component (C) is a mixture of salts at least one of which has hydrocarbyl groups consisting wholly of secondary alkyl groups containing 6 carbon atoms.

7. The oil composition according to any of the preceding claims wherein component (C) includes a dialkyl phosphorodithioic acid metal salt in which the alkyl groups are 4-methyl-2-pentyl groups.

8. The oil composition according to any one of the preceding claims in which the metal of component (C) is zinc.

9. The oil composition according to any one of the preceding claims in which the ashless dispersant has a polymer backbone comprising an ethylene alpha-olefin copolymer.

10. The oil composition according to claim 9 in which the backbone polymer of the dispersant has been produced using a metallocene catalyst.

11. The oil composition according to either claim 9 or claim 10 in which the ashless dispersant contains polar nitrogen-containing groups.

12. The oil composition according to any one of claims 9 to 11 in which the number average molecular weight of the polymer is between 1600 and 3500.

13. The oil composition according to any of claims 1 to 8 in which the polymer backbone of the ashless dispersant is poly(isobutylene).

14. The oil composition according to any of claims 9, 10, 12 or 13 in which the polymer backbone is substituted with a succinic anhydride group.

15. The oil composition according to either claim 13 or claim 14 in which the ashless dispersant contains polar nitrogen-containing groups.

16. The oil composition according to claim 13 in which the polymer backbone is substituted with a succinic anhydride group, the ashless dispersant contains polar nitrogen-containing groups and the number average molecular weight of the polymer backbone is between 1000 and 2500.

17. The oil composition according to claim 16 in which the number average molecular weight of the polymer backbone is between 1300 and 2500.

18. A lubricating oil concentrate comprising 3 to 60 weight percent of component (B) and 1 to 20 weight percent of component (C) in a base oil of lubricating viscosity, wherein components (B) and (C) are defined as in claim 1.

19. The use in a lubricating oil composition of a dihydrocarbyl phosphorodithioic acid metal salt wherein at least 70 mole % of the hydrocarbyl groups are secondary alkyl groups of 6 carbon atoms, no more than 15 mole % of the hydrocarbyl groups are primary groups and no more than 15 mole % of the hydrocarbyl groups are secondary alkyl groups of less than 6 carbon atoms, and the metal of the salt is selected from alkali metal, alkaline earth metal, aluminum, lead, tin, molybdenum, manganese, nickel, copper and zinc, for improving the wear protection of spark-ignited and diesel engines under low temperature conditions.

20. The use according to claim 19 wherein the hydrocarbyl groups are secondary alkyl groups, at least 70 mole % of which are secondary alkyl groups of 6 carbon atoms, no more than 15 mole % are primary alkyl groups, and no more than 15 mole % are secondary alkyl groups having less than 6 carbon atoms.

21. The use in spark-ignited or diesel engines of a lubricating oil composition as defined in claim 1 for improving the wear protection of said spark-ignited or diesel engines.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 98/01899

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10M141/10 //(C10M141/10,133:56,137:10),C10N30:06,C10N40:25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 302378 A (NIPPON OIL CO LTD), 19 November 1996, see abstract	1-8, 13-21
E	& US 5 744 430 A (HIRATA ET AL) 28 April 1998 see tables 1,2 ---	1-8, 13-21
X	EP 0 113 045 A (HONDA MOTOR CO LTD; IDEMITSU KOSAN CO LTD) 11 July 1984 cited in the application see examples 2,16,21; table 1 ---	1-8, 13-21
A	GB 1 365 311 A (OROBIS LTD) 29 August 1974 see example A --- -/--	1,13-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 9 July 1998	Date of mailing of the international search report 20/07/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Kazemi, P

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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