(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 April 2009 (02.04.2009)

PCT

(10) International Publication Number
WO 2009/042590 A1

(51) International Patent Classification:
C10M 163/00 (2006.01)

(21) International Application Number:
PCT/US2008/077371

(22) International Filing Date:
23 September 2008 (23.09.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/975,351 26 September 2007 (26.09.2007) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report*

WO 2009/042590 A1

(54) Title: TITANIUM COMPOUNDS AND COMPLEXES AS ADDITIVES IN LUBRICANTS

(57) Abstract: A lubricating composition comprising an oil of lubricating viscosity, at least 25 parts per million by weight of titanium in the form of an oil-soluble titanium-containing material, and at least 70 parts per million boron in the form of a soluble boron compound such as a borate ester provides beneficial effects on properties such as deposit control, oxidation, and filterability in engine oils and lubrication of engines.

TITLE

Titanium Compounds and Complexes as Additives in Lubricants

BACKGROUND OF THE INVENTION

[0001] The present invention relates to lubricant compositions containing a soluble titanium-containing material, having beneficial effects on properties such as deposit control, oxidation, and filterability in, for instance, engine oils.

[0002] Current and proposed specifications for crankcase lubricants, such as GF-4 for passenger car motor oils, and PC-10 for heavy duty diesel engines specify increasingly stringent standards to meet government specifications. Of particular concern are sulfur and phosphorus limits. It is widely believed that lowering these limits may have a serious impact on engine performance, engine wear, and oxidation of engine oils. This is because historically a major contributor to phosphorus content in engine oils has been zinc dialkyldithiophosphate (ZDP), and ZDP has long been used to impart antiwear and antioxidancy performance to engine oils. Thus, as reduced amounts of ZDP are anticipated in engine oils, there is a need for alternatives to impart protection against deterioration in one or more of the properties of engine performance, engine wear, and oxidation of engine oils. Such improved protection is desirable whether or not ZDP and related materials are included in the lubricant. Desirable lubricants may be low in one or more of phosphorus, sulfur, and ash, that is, sulfated ash according to ASTM D-874 (a measure of the metal content of the sample).

[0003] U.S. Patent 6,624,187, Schwind et al., November 4, 2003, discloses lubricating compositions, concentrates, and greases containing the combination of an organic polysulfide and an overbased composition or a phosphorus or boron compound. Metals which can be used in the basic metal compound include (among others) titanium.

[0004] U.S. Patent 5,968,880, Mathur et al., October 19, 1999, discloses lubricating composition, functional fluids and greases containing certain thiophosphorus esters. Boron antiwear or extreme pressure agents can be present, which can be a borated overbased metal salt. Examples of the metals of the basic metal compound include (among others) titanium.

[0005] U.S. Patent 5,811,378, Lange, September 22, 1998, discloses metal containing dispersant viscosity improvers for lubricating oils, comprising the reaction product of a hydrocarbon polymer grafted with an α,β-unsaturated carboxylic acid and a nitrogen and metal containing derivative of a hydrocarbon substituted polycarboxylic acid. The metal can be selected from (among others) titanium.

[0006] U.S. Patent 5,614,480, Salomon et al., March 25, 1997, discloses lubricating compositions and concentrates including an oil of lubricating viscosity, a carboxylic derivative, and an alkali metal overbased salt. Also disclosed are antioxidants which can be an oil-soluble transition metal-containing composition. The transition metal can be selected from (among others) titanium.

[0007] Titanium in the form of surface-modified TiO_2 particles has also been disclosed as an additive in liquid paraffin for imparting friction and wear properties. See, for instance, Q. Xue et al., *Wear* 213, 29-32, 1997.

[0008] U.S. Patent Publication US 2006-0217271, Brown et al., September 28, 2006, discloses titanium complexes as additives in lubricants. Lubricant compositions comprise an oil of lubricating viscosity, 1 to 1000 ppm (alternatively, 1 to less than 50 ppm) titanium in the form of an oil-soluble titanium-containing material, and at least one additive selected from the group consisting of antiwear agents, dispersants, antioxidants, and detergents.

[0009] U.S. Patent Publications US 2006-0014561, Esche et al., January 19, 2006, and US 2007-0149418, Esche et al., June 28, 2007, each disclose a lubricated surface containing a base oil and an amount of a hydrocarbon soluble titanium compound effective to provide a reduction in surface wear.

[0010] It has now been discovered that the presence of titanium, supplied, for instance, in combination with certain levels of boron, provides a beneficial effect on one or more of the above properties. In particular, such materials impart a beneficial effect in one or more of the Komatsu Hot Tube Deposits screen test (KHT), the KES Filterability test, the Dispersant Panel Coker test (a test used to evaluate the deposit-forming tendency of an engine oil), the Cat 1M-PC test, and the PDSC oil induction time test.

SUMMARY OF THE INVENTION

[0011] The present invention provides a method for lubricating an internal combustion engine, comprising supplying to said engine a lubricating composition comprising:

(a) an oil of lubricating viscosity;

(b) at least about 25 parts per million by weight of titanium in the form of an oil-soluble titanium-containing material;

(c) an antioxidant other than a Ti-containing antioxidant,

(d) a metal containing detergent other than a Ti-containing detergent, and

(e) at least about 70 parts per million by weight of boron in the form of a soluble boron compound such as a borate ester.

[0012] The invention further provides a lubricating composition comprising:

(a) an oil of lubricating viscosity;

(b) at least about 25 parts per million by weight of titanium in the form of an oil-soluble titanium-containing material;

(c) an antioxidant other than a Ti-containing antioxidant,

(d) a metal containing detergent other than a Ti-containing detergent, and

(e) at least about 70 parts per million by weight of boron in the form of a soluble boron compound such as a borate ester.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0014] One element of the present invention is an oil of lubricating viscosity, also referred to as a base oil. The base oil used in the inventive lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)		Saturates(%)	Viscosity Index
Group I	>0.03	and/or	<90	80 to 120
Group II	<0.03	and	>90	80 to 120
Group III	<0.03	and	>90	>120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III or IV			

Groups I, II and III are mineral oil base stocks. The oil of lubricating viscosity, then, can include natural or synthetic lubricating oils and mixtures thereof. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and polyester oils, are often used.

[0015] Natural oils include animal oils and vegetable oils (e.g. castor oil, lard oil and other vegetable acid esters) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Hydrotreated or hydrocracked oils are included within the scope of useful oils of lubricating viscosity.

[0016] Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, (e.g., biphenyls, terphenyls, and alkylated polyphenyls), alkylated diphenyl ethers and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof.

[0017] Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, for example, esterification or etherification, constitute other classes of known synthetic lubricating oils that can be used.

[0018] Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids and those made from C5 to C12 monocarboxylic acids and polyols or polyol ethers. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as the poly-alkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils.

[0019] Hydrotreated naphthenic oils are also known and can be used, as well as oils prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure followed by hydroisomerization.

[0020] Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. 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. 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 often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0021] The present invention also comprises titanium in the form of an oil-soluble titanium-containing material or, more generally, a hydrocarbon-soluble material. By “oil-soluble” or “hydrocarbon soluble” is meant a material which will dissolve or disperse on a macroscopic or gross scale in an oil or hydrocarbon, as the case may be, typically a mineral oil, such that a practical solution or dispersion can be prepared. In order to prepare a useful lubricant formulation, the titanium material should not precipitate or settle out over a course of several days or weeks. Such materials may exhibit true solubility on a molecular scale or may exist in the form of agglomerations of varying size or scale, provided however that they have dissolved or dispersed on a gross scale.

[0022] The nature of the oil-soluble titanium-containing material can be diverse. Such materials are described, for example, in U.S. Patent Publication US 2006-0217271, Brown et al. Among the titanium compounds that may be used in – or which may be used for preparation of the oils-soluble materials of – the present invention are various Ti (IV) compounds such as titanium (IV) oxide; titanium (IV) sulfide; titanium (IV) nitrate; titanium (IV) alkoxides such as titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, titanium butoxide, or titanium 2-ethylhexoxide; and other titanium compounds or complexes including but not limited to titanium phenates; titanium carboxylates such as titanium (IV) 2-ethyl-1-3-hexanedioate or titanium citrate or titanium oleate; titanium (IV) 2-ethylhexanoate; and titanium (IV) (triethanolaminato)isopropoxide. Other forms of titanium encompassed within the present invention include titanium phosphates such as titanium dithiophosphates (e.g., dialkyldithiophosphates) and titanium sulfonates (e.g., alkylsulfonates), or, generally, the reaction product of titanium compounds with various acid materials to form salts, especially oil-soluble salts. Titanium compounds can thus be derived from, among others, organic acids, alcohols, and glycols. Ti compounds may also exist in dimeric or oligomeric form, containing Ti–O–Ti structures. Such titanium materials are commercially available or can be readily prepared by appropriate synthesis techniques which will be apparent to the person skilled in the art. They may exist at room temperature as a solid or a liquid, depending on the particular compound. They may also be provided in a solution form in an appropriate inert solvent.

[0023] In another embodiment, the titanium can be supplied as a Ti-modified dispersant. Dispersants are described in greater detail below. An example of a dispersant is a succinimide dispersant. Such materials may be prepared by forming a titanium mixed anhydride between a titanium alkoxide and a hydrocarbyl-substituted succinic anhydride, such as an alkenyl- (or alkyl) succinic anhydride. The resulting titanate-succinate intermediate may be used directly or it may be reacted with any of a number of materials, such as (a) a polyamine-based succinimide/amide dispersant having free, condensable –NH functionality; (b) the components of a polyamine-based succinimide/amide dispersant, i.e., an alkenyl- (or alkyl-)succinic anhydride and a polyamine, (c) a hydroxy-containing polyester dispersant prepared by the reaction of a substituted succinic anhydride with a polyol, aminoalcohol, polyamine, or mixtures thereof. Alternatively, the titanate-succinate intermediate may be reacted with other agents such as alcohols, aminoalcohols, ether alcohols, polyether alcohols or polyols, or fatty acids, and the product thereof either used directly to impart Ti to a lubricant, or else further reacted with the succinic dispersants as described above. As an example, 1 part (by mole) of tetraisopropyl titanate (that is, titanium isopropoxide) may be reacted with 2 parts (by mole) of a polyisobutene-substituted succinic anhydride at 140-150 °C for 5 to 6 hours to provide a titanium modified dispersant or intermediate. The resulting material (30 g) may be further reacted with a succinimide dispersant from polyisobutene-substituted succinic anhydride and a polyethylenepolyamine mixture (127 g + diluent oil) at 150 °C for 1.5 hours, to produce a titanium-modified succinimide dispersant.

[0024] In another embodiment, the titanium can be supplied as a tolyltriazole oligomer salted with and/or chelated to titanium. The surface active properties of the tolyltriazole allow it to act as a delivery system for the titanium, imparting both the titanium performance benefits as elsewhere described herein, as well as anti-wear performance of tolyltriazole. In one embodiment, this material can be prepared by first combining tolyltriazole (1.5 eq) and formaldehyde (1.57 eq) in an inert solvent followed by addition of diethanolamine (1.5 eq) and then hexadecyl succinic anhydride (1.5 eq) and a catalytic amount of methanesulfonic acid, while heating and removing water of condensation. This material may be referred to as the “oligomer.” This intermediate can be reacted with titanium isopropoxide (0.554 eq) at 60°C, followed by vacuum stripping to provide a red viscous product.

[0025] Other forms of titanium can also be provided, such as surface-modified titanium dioxide nanoparticles, as described in greater detail in Q. Xue et al., Wear 213, 29-32, 1997 (Elsevier Science S.A.), which discloses TiO2 nanoparticles with an average diameter of 5 nm, surface modified with 2-ethylhexanoic acid. Such nanoparticles capped by an organic hydrocarbyl chain are said to disperse well in non-polar and weakly polar organic solvents. Their synthesis is described in greater detail by K.G. Severin et al. in Chem. Mater. 6, 8990-898, 1994.

[0026] In one embodiment, the titanium is not a part of or affixed to a long-chain polymer, that is, a high molecular weight polymer. Thus, the titanium species may, in these circumstances, have a number average molecular weight of less than 150,000 or less than 100,000 or 30,000 or 20,000 or 10,000 or 5000, or 3000 or 2000, e.g., about 1000 or less than 1000. Non-polymeric species providing the titanium as disclosed above will typically be below the molecular weight range of such polymers. For example, a titanium tetraalkoxide such as titanium isopropoxide may have a number average molecular weight of 1000 or less, or 300 or less, as may be readily calculated. A titanium-modified dispersant, as described above, may include a hydrocarbyl substituent with a number average molecular weight of 3000 or less or 2000 or less, e.g., about 1000.

[0027] The amount of titanium present in the lubricant is typically at least 25 parts per million by weight (as the metal Ti). Such amounts, in combination with the amounts of boron, described below, are believed to impart significantly improved oxidation stability to the lubricant in which they are employed. The amount of titanium may also be at least 50 or at least 75 parts per million. Suitable amounts of titanium thus include 75 to 1000 ppm, or 85 to 500 or to 250 or to 200 or to 150 ppm.

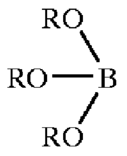
[0028] These amounts may vary with the particular system investigated and may be influenced to some extent by the anion or complexing agent associated with the titanium. Also, the overall amount of the particular titanium compound to be employed will depend on the relative weight of the anionic or complexing groups associated with the titanium. Titanium isopropoxide, for instance, is typically commercially supplied in a form which contains 16.8% titanium by weight. Thus, if amounts of 85 to 150 ppm of titanium are to be provided, about 506 to about 893 ppm (that is, about 0.05 to about 0.09 percent by weight) of titanium isopropoxide would be used, and so on.

[0029] Likewise, different performance advantages may be obtained by using different specific titanium compounds, that is, with different anionic portions or complexing portions of the compound. For example, surface-modified TiO_2 particles may impart friction and wear properties. Similarly, tolyltriazole oligomers salted with and/or chelated to titanium may impart antiwear properties. In a like manner, titanium compounds containing relatively long chain anionic portions or anionic portion containing phosphorus or other anti-wear elements may impart anti-wear performance by virtue of the anti-wear properties of the anion. Examples would include titanium neodecanoate; titanium 2-ethylhexoxide; titanium (IV) 2-propanolato, tris-isooctadecanato-O; titanium (IV) 2,2(bis-2-prepenolatomethyl)butanolato, tris-neodecanato-O; titanium (IV) 2-propanolato, tris(dioctyl)phosphato-O; and titanium (IV) 2-propanolato, tris(dodecyl)benzenesulfanato-O. When any such anti-wear-imparting materials are used, they may be used in an amount suitable to impart – and should in fact impart – a reduction in surface wear greater than surface of a lubricant composition devoid of such compound

[0030] In certain embodiments, the titanium-containing material may be selected from the group consisting of titanium alkoxides, titanium modified dispersants, titanium salts of aromatic carboxylic acids (such as benzoic acid or alkyl-substituted benzoic acids), and titanium salts of sulfur-containing acids (such as those of the formula R-S-R'-CO_2H, where R is a hydrocarbyl group and R' is a hydrocarbylene group).

[0031] The titanium compound can be imparted to the lubricant composition in any convenient manner, such as by adding to the otherwise finished lubricant (top-treating) or by pre-blending the titanium compound in the form of a concentrate in an oil or other suitable solvent, optionally along with one or more additional components such as an antioxidant, a friction modifier such as glycerol monooleate, a dispersant such as a succinimide dispersant, or a detergent such as an overbased sulfurized phenate detergent. Such additional components, typically along with diluent oil, may typically be included in an additive package, sometimes referred to as a DI (detergent-inhibitor) package.

[0032] The compositions of the present invention will also contain boron in the form of a soluble boron compound such as a borate ester. The borate ester (also known as a borated ester antiwear agent), may be one or more compounds represented by one or more of the formulas



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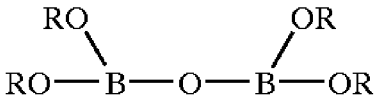

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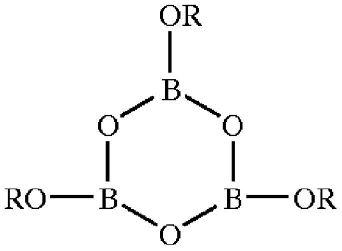
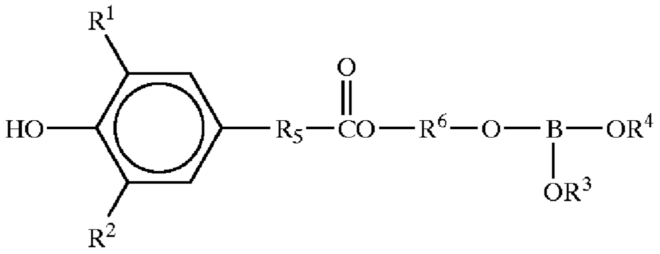


wherein each R may be independently an organic group and any two adjacent R groups may together form a cyclic group. Such materials may be the product of boric acid with an alcohol. Mixtures of two or more of the foregoing may be used. In one embodiment, each R may be independently a hydrocarbyl group. The total number of carbon atoms in the R groups in each formula may be sufficient to render the compound soluble in the base oil. Generally, the total number of carbon atoms in the R groups may be at least 8, and in one embodiment at least 10, and in one embodiment at least 12. There may be no limit to the total number of carbon atoms in the R groups that is required, but a practical upper limit may be 400 or 500 carbon atoms. In one embodiment, each R group may be independently a hydrocarbyl group of 1 to 100 carbon atoms, and in one embodiment 1 to 50 carbon atoms, and in one embodiment 1 to 30 carbon atoms, and in one embodiment 1 to 10 carbon atoms, with the proviso that the total number of carbons in the R group may be at least 8. Each R group may be the same as the other, although they may be different. Examples of useful R groups may include isopropyl, n-butyl, isobutyl, amyl, 1,3 dimethyl-butyl, 2-ethyl-1-hexyl (e.g., from 2-ethylhexanol), isooctyl, decyl, dodecyl, tetradecyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphthyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, and alkylnaphthylalkyl.

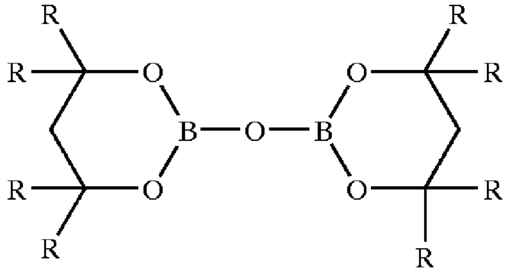
[0033] In one embodiment, the borate ester may be a compound represented by the formula



wherein R_1, R_2, R_3 and R_4 are independently hydrocarbyl groups of 1 to 12 carbon atoms; and R_5 and R_6 are independently alkylene groups of 1 to 6 carbon atoms, and in one embodiment 2 to 4 carbon atoms, and in one embodiment 2 or 3 carbon atoms. In one embodiment, R_1 and R_2 may independently contain 1 to 6 carbon atoms, and in one embodiment each may be a t-butyl group. In one embodiment, R_3 and R_4 are independently hydrocarbyl groups of 2 to 12 carbon atoms, and in one embodiment 8 to 10 carbon atoms. In one embodiment, R_5 and R_6 are independently $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$.

[0034] A useful borate ester may be available from Crompton Corporation under the trade designation LA-2607. This material may be identified as a phenolic borate having the structure represented above wherein R^1 and R^2 are each t-butyl, R^3 and R^4 are hydrocarbyl groups of 2 to 12 carbon atoms, R^5 is $-CH_2CH_2-$, and R^6 is $-CH_2CH_2CH_2-$.

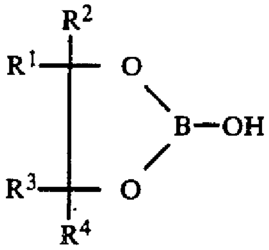
[0035] In one embodiment, the borate ester may be a compound represented by the formula:



wherein the R groups are independently hydrogen or hydrocarbyl groups. Each of the hydrocarbyl groups may contain 1 to 12 carbon atoms, and in one embodiment 1 to 4 carbon atoms. An example is 2,2'-oxy-bis-(4,4,6-trimethyl-1,3,2-dioxaborinane).

[0036] In one embodiment, the borate ester may be a compound represented by the formula $B(OC_5H_{11})_3$ or $B(OC_4H_9)_3$. A useful boron-containing compound may be available from Mobil under the trade designation MCP-1286.

[0037] Other borate esters include borated epoxides, so termed because they may be prepared by reacting an epoxide with a boron source. Such materials may be represented by the formula



among other structures, where the Rs are hydrogen or hydrocarbyl groups. Borated epoxides are generally the reaction product of one or more reactive boron compounds such as boric acid or boron trioxide or certain borate esters with at least one epoxide. The epoxide is generally an aliphatic epoxide having 8 to 30, or 10 to 24, or 12 to 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl epoxide, octyl epoxide, oleyl epoxide and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having 14 to 16 carbon atoms and 14 to 18 carbon atoms. The borated fatty epoxides are generally known and are disclosed in U.S. Patent 4,584,115

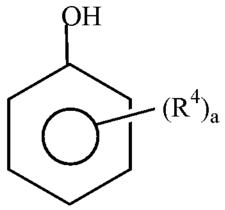
[0038] The borate compound will typically be employed in the lubricating oil composition at a sufficient concentration to provide the lubricating oil composition with a boron concentration (as B) of at least 70 parts per million by weight. Such amounts are believed to impart superior oxidation performance when combined with the titanium compound as described above. Suitable ranges for the boron may include 70 to 1000 ppm or 85 to 500 or to 250 or to 200 or to 150 ppm.

[0039] Other types of boron compounds include borated dispersants such as those described in greater detail in U.S. Patent 6,596,672, see columns 13 and 14, as well as in U.S. Patents 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662 and 4,925,983.

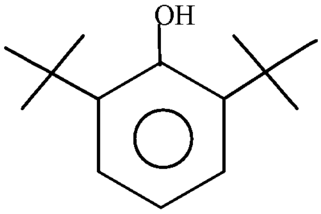
[0040] The foregoing components may be added directly to the lubricating oil composition. In one embodiment, however, they may be diluted with a substantially inert, normally liquid organic diluent such as mineral oil, synthetic oil (e.g., ester of dicarboxylic acid), naptha, alkylated (e.g. C_{10}-C_{13} alkyl) benzene, toluene, or xylene to form an additive concentrate. These concentrates may contain 1% to 99% by weight, and in one embodiment 10% to 90% by weight of the diluent.

[0041] Another component in the formulations of the present invention is an antioxidant. While certain antioxidants may contain titanium, this component is intended to be other than a titanium-containing antioxidant. That is, although a Ti-containing antioxidant may or may not be present in the lubricant, in such instances a different or additional antioxidant will be present which does not contain titanium.

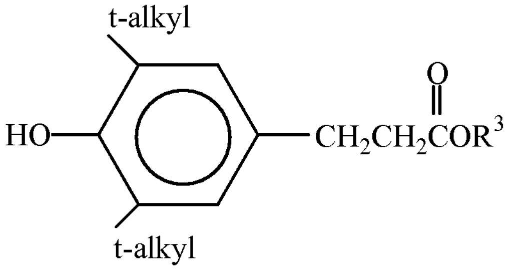
[0042] Antioxidants encompass phenolic antioxidants, which may be of the general the formula



wherein R^4 is an alkyl group containing 1 to 24, or 4 to 18, carbon atoms and a is an integer of 1 to 5 or 1 to 3, or 2. The phenol may be a butyl substituted phenol containing 2 or 3 t-butyl groups, such as

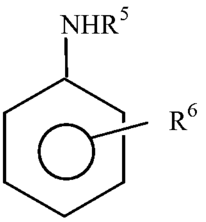


The para position may also be occupied by a hydrocarbyl group or a group bridging two aromatic rings. In certain embodiments the para position is occupied by an ester-containing group, such as, for example, an antioxidant of the formula

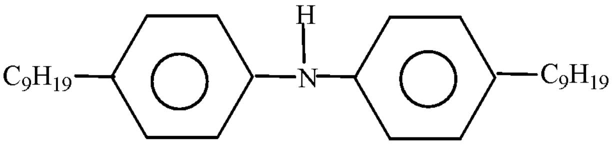


wherein R^3 is a hydrocarbyl group such as an alkyl group containing, e.g., 1 to 18 or 2 to 12 or 2 to 8 or 2 to 6 carbon atoms; and t-alkyl can be t-butyl. Such antioxidants are described in greater detail in U.S. Patent 6,559,105.

[0043] Antioxidants also include aromatic amines, such as those of the formula



wherein R^5 can be an aromatic group such as a phenyl group, a naphthyl group, or a phenyl group substituted by R^7, and R^6 and R^7 can be independently a hydrogen or an alkyl group containing 1 to 24 or 4 to 20 or 6 to 12 carbon atoms. In one embodiment, an aromatic amine antioxidant can comprise an alkylated diphenylamine such as nonylated diphenylamine of the formula



or a mixture of a di-nonylated and a mono-nonylated diphenylamine.

[0044] Antioxidants also include sulfurized olefins such as mono-, or disulfides or mixtures thereof. These materials generally have sulfide linkages having 1 to 10 sulfur atoms, for instance, 1 to 4, or 1 or 2. Materials which can be sulfurized to form the sulfurized organic compositions of the present invention include oils, fatty acids and esters, olefins and polyolefins made thereof, terpenes, or Diels-Alder adducts. Details of methods of preparing some such sulfurized materials can be found in U.S. Pat. Nos. 3,471,404 and 4,191,659.

[0045] Molybdenum compounds can also serve as antioxidants, and these materials can also serve in various other functions, such as antiwear agents. The use of molybdenum and sulfur containing compositions in lubricating oil compositions as antiwear agents and antioxidants is known. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition prepared by (1) combining a polar solvent, an acidic molybdenum compound and an oil-soluble basic nitrogen compound to form a molybdenum-containing complex and (2) contacting the complex with carbon disulfide to form the molybdenum and sulfur containing composition. A molybdenum based antioxidant may be present or may be absent. In certain embodiments, the lubricant formulation contains little or no molybdenum, for instance, less than 500, or less than 300 or less than 150 or less than 100 or less than 50 or less than 20 or less than 10 or less than 5 or less than 1 parts per million Mo by weight.

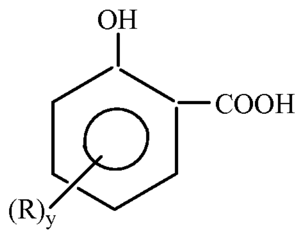
[0046] Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5 percent by weight or 0.15 to 4.5 percent or 0.2 to 4 percent or 0.4 to 3 percent. These amounts may be the amount of a single antioxidant (e.g., an aromatic amine antioxidant) or of multiple antioxidants. Additionally, more than one antioxidant may be present, and certain combinations of these can be synergistic in their combined overall effect.

[0047] Another component is a metal containing detergent other than a Ti-containing detergent. Once again, this does not mean that no titanium-containing detergent is present or that the titanium compound described above may not be in the form of a detergent. Rather, it means that the detergent will be other than any Ti-containing detergent. Detergents are typically overbased materials, although they may also be neutral salts. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base (such as a Ca, Mg, Ba, Na, or K compound, among other metals), and a promoter such as a phenol or alcohol. The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0048] Such overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of sulfonic acids such as long chain alkylbenzenesulfonic acids, carboxylic acids, phenols, including overbased phenol sulfides (sulfur-bridged phenols), phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109.

[0049] Detergents based on other, or more specific, acidic substrates include salicylates, salixarates, and saligenins. Typical salicylate detergents are metal overbased salicylates having a sufficiently long hydrocarbon substituent to promote oil solubility. Hydrocarbyl-substituted salicylic acids can be prepared by the reaction of the corresponding phenol by reaction of an alkali metal salt thereof with carbon dioxide. The hydrocarbon substituent can be as described for the carboxylate or phenate detergents.

[0050] More particularly, hydrocarbon-substituted salicylic acids may be represented by the formula



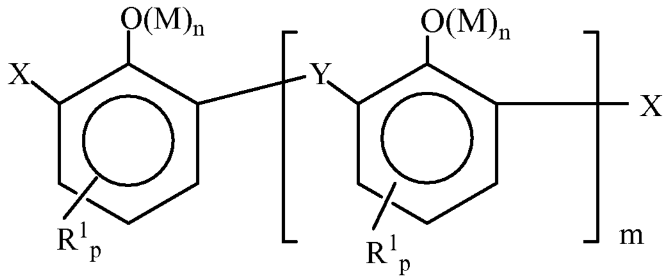
(C-1

wherein each R is an aliphatic hydrocarbyl group, and y is independently 1, 2, 3 or 4, with the proviso that R and y are such that the total number of carbon atoms provided by the R groups is at least 7 carbon atoms. In one embodiment, y is 1 or 2, and in one embodiment y is 1. The total number of carbon atoms provided by the R groups may be 7 to 50, and in one embodiment 12 to 50, and in one embodiment 12 to 40, and in one embodiment 12 to 30, and in one embodiment 16 to 24, and in one embodiment 16 to 18, and in one embodiment 20 to 24. In one embodiment, y is 1 and R is an alkyl group containing 16 to 18 carbon atoms. Overbased salicylic acid detergents and their preparation are described in greater detail in U.S. Pat. No. 3,372,116.

[0051] In one embodiment, the metal salt is "M7101" which is a product supplied by Infineum USA LP identified as a calcium salicylate dispersed in oil having a TBN of 168, a calcium content of 6.0% by weight, an a diluent oil concentration of 40% by weight.

[0052] In certain embodiments, the use of salicylate detergents may be beneficial. Salicylate detergents are sulfur-free and as such and may be favored in reducing the amount of sulfur present in the lubricant. Moreover, it has been observed that even very low levels of titanium (e.g., 20 ppm) can reduce deposit formation in formulations containing mainly salicylate detergent. This same level of titanium may be less effective or ineffective in similar formulations containing mainly sulfonate, phenate, or salixarate detergents.

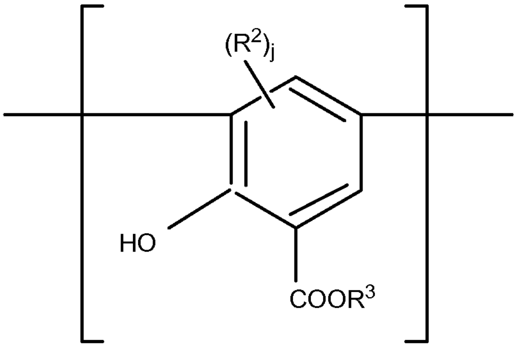
[0053] Salixarate and saligenin derivative detergents are described in greater detail in US Published Application 2004/0102335. Saligenin detergents can be represented by the formula:



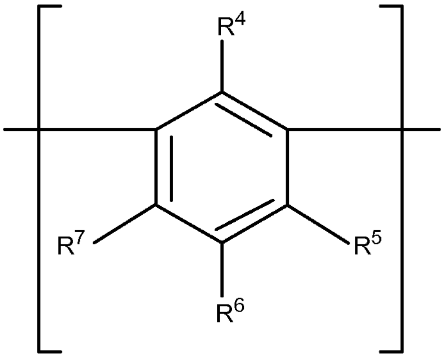
wherein X comprises -CHO or -CH_2OH, Y comprises -CH_2- or -CH_2OCH_2-, and wherein, in typical embodiments, such -CHO groups comprise at least 10 mole percent of the X and Y groups; and M is a valence of a metal ion, typically mono- or di- valent. Each n is independently 0 or 1. R1 is a hydrocarbyl group typically containing 1 to 60 carbon atoms, m is 0 to 10, and when m > 0, one of the X groups can be H; each p is independently 0, 1, 2 or 3, preferably 1; and that the total number of carbon atoms in all R^1 groups is typically at least 7.

When n is 0, M is replaced by H to form an unneutralized phenolic –OH group. Preferred metal ions M are monovalent metals ion such as lithium, sodium, potassium, as well as divalent ions such as calcium or magnesium. Saligenin derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,310,009.

[0054] Salixarate detergents (an example, along with salicylate detergents, of a detergent containing a salicylate moiety) can be represented by a substantially linear compound comprising at least one unit of formula (I) or formula (II):

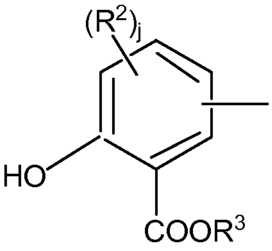


(I)

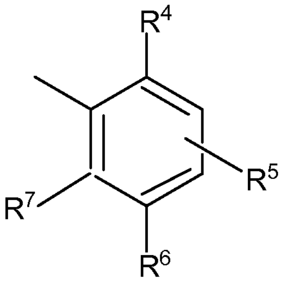


(II)

each end of the compound having a terminal group of formula (III) or formula (IV):



(III)



(IV)

such groups being linked by divalent bridging groups A, which may be the same or different for each linkage. In the above formulas (I)-(IV) R^3 is hydrogen or a hydrocarbyl group; R^2 is hydroxyl or a hydrocarbyl group, and j is 0, 1, or 2; R^6

is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; and either R^4 is hydroxyl and R^5 and R^7 are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R^5 and R^7 are both hydroxyl and R^4 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; provided that at least one of R^4, R^5, R^6 and R^7 is hydrocarbyl containing at least 8 carbon atoms; and wherein the molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is 0.1:1 to 2:1. The divalent bridging group "A," which may be the same or different in each occurrence, includes -CH_2- (methylene bridge) and -CH_2OCH_2- (ether bridge), either of which may be derived from formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin). Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0055] The amount of the detergent can typically be 0.1 to 5.0 percent by weight on an oil free basis. Since many detergents contain 30-50 percent diluent oil, this would correspond to, for instance, about 0.2 to 12 percent by weight of the commercially available, oil-diluted detergents. In other embodiments, the amount of detergent can be 0.2 to 4.0 percent by weight or 0.3-3.0 percent by weight (oil-free). These amounts may be the amount of a single detergent or of multiple detergents.

[0056] It will be evident that the detergent may be based on any of the aforementioned metals as well as other metals generally. Thus, titanium based detergents are also possible. Thus, while certain detergents may contain titanium, the detergent as specified herein is other than a titanium-containing detergent. That is, although a Ti-containing detergent may or may not be present in the lubricant, if it is present, a different, or additional detergent will be present which does not contain titanium. Of course, it is recognized that the metal ions within a lubricant may migrate from one detergent to another, so that if a detergent other than a titanium detergent is initially added, after a period of time some of the molecules thereof may become associated with a Ti ion. The presence of a detergent other than a Ti-containing detergent is to be interpreted as not to be negated by the presence of such incidental, transferred Ti ions in such detergent.

[0057] Additional components may be used in preparing a lubricant according to the present invention, for instance, those additives typically employed in a crankcase lubricant. Crankcase lubricants may typically contain any or all of the following components hereinafter described.

[0058] One such additive is an antiwear agent, other than, or in addition to, the above described boron compound.. Examples of such anti-wear agents include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. The phosphorus acids include phosphoric, phosphonic, phosphinic, and thiophosphoric acids including dithiophosphoric acid as well as monothiophosphoric acids, thiophosphinic acids, and thiophosphonic acids. Non-phosphorus-containing antiwear agents include molybdenum-containing compounds, and sulfurized olefins.

[0059] Phosphorus-containing anti-wear agents include phosphorus acid esters, which can be prepared by reacting one or more phosphorus acids or anhydrides with an alcohol containing, for instance, 1 to 30 or 2 to 24 or to 12 carbon atoms, including monools and diols and polyols of various types. Such alcohols, including commercial alcohol mixtures, are well known. Examples of these phosphorus acid esters include triphenylphosphate and tricresylphosphate.

[0060] In one embodiment, the phosphorus antiwear/extreme pressure agent can be a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula $(RO)_2PSSH$ wherein each R is independently a hydrocarbyl group containing, e.g., 3 to 30 carbon atoms, or up to 18, or 12, or 8 carbon atoms.

[0061] Metal salts of the phosphorus acid esters are prepared by the reaction of a metal base with a phosphorus acid ester. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, and borates. The metals of the metal base include Group IA, IIA, IB through VIIB, and VIII metals (CAS version of the Periodic Table of the Elements). These metals include the alkali metals, alkaline earth metals and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. In one embodiment, the metal is magnesium, calcium, manganese or zinc. The metal may also be titanium, although in certain embodiments the metal salt is other than a Ti salt.

[0062] In one embodiment, phosphorus containing antiwear/extreme pressure agent is a metal thiophosphate, or a metal dithiophosphate. The metal thiophosphate is prepared by means known to those in the art. Examples of metal dithiophosphates include zinc isopropyl methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, zinc di(cyclohexyl) dithiophosphate, zinc isobutyl 2-ethylhexyl dithiophosphate, zinc isopropyl 2-ethylhexyl dithiophosphate, zinc isobutyl isoamyl dithiophosphate, zinc isopropyl n-butyl dithiophosphate, calcium di(hexyl) dithiophosphate, and barium di(nonyl) dithiophosphate.

[0063] In one embodiment, the phosphorus containing antiwear agent is a phosphorus containing amide. The phosphorus containing amides may be, for instance prepared by the reaction of a thiophosphoric or dithiophosphoric acid ester with an unsaturated amide. Examples of unsaturated amides include acrylamide, N,N-methylene bis(acrylamide), methacrylamide, crotonamide, and the like. The reaction product of the phosphorus acid and the unsaturated amide may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The phosphorus containing amides are known in the art and are disclosed in U.S. Pat. Nos. 4,670,169, 4,770,807, and 4,876,374.

[0064] In one embodiment, the phosphorus antiwear/extreme pressure agent is a phosphorus containing carboxylic ester contain at least one phosphite. The phosphite may be a di- or trihydrocarbyl phosphite. In one embodiment, each hydrocarbyl group independently contains 1 to 24 carbon atoms, or 1 to 18 or 2 to 8 carbon atoms. Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutyl hydrogen phosphite, dioleyl hydrogen phosphite, di(C_{14-18}) hydrogen phosphite, and triphenyl phosphite.

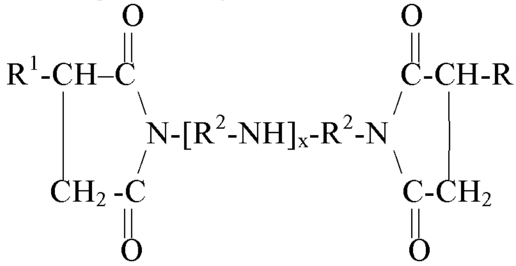
[0065] Other phosphorus-containing antiwear agents include triphenylthiophosphate, and dithiophosphoric acid ester such as mixed O,O-(2-methylpropyl, amyl)-S-carbomethoxy-ethylphosphorodithioates and O,O-diisooctyl-S-carbomethoxyethyl-phosphorodithioate.

[0066] Such phosphorus-containing antiwear agents are described in greater detail in U.S. Published Application 2003/0092585.

[0067] The appropriate amount of the phosphorus-containing antiwear agent will depend to some extent on the particular agent selected and its effectiveness. However, in certain embodiments it may be present in an amount to deliver 0.01 to 0.2 weight percent phosphorus to the composition, or to deliver 0.015 to 0.15 or 0.02 to 0.1 or 0.025 to 0.08 percent phosphorus. For dibutyl phosphite, for instance ($(C_4H_9O)_2P(O)H$), which contains about 16 weight percent P, appropriate amounts may thus include 0.062 to 0.56 percent. For a typical zinc dialkyldithiophosphate (ZDP), which may contain 11 percent P (calculated on an oil free basis), suitable amounts may include 0.09 to 0.82 percent. It is believed that the benefits of the present invention may sometimes be more clearly realized in those formulations containing relatively low amounts of ZDP and other sources of zinc, sulfur, and phosphorus, for instance, less than 1200, 1000, 500, 100, or even 50 ppm phosphorus. In certain embodiments the amount of phosphorus can be 50 to 500 ppm or 50 to 600 ppm.

[0068] Other antiwear agents may include dithiocarbamate compounds. In one embodiment, the dithiocarbamate containing composition is derived from the reaction product of a diamylamine or dibutylamine with carbon disulfide which forms a dithiocarbamic acid or a salt which is ultimately reacted with an acrylamide. The amount of this agent, or of the antiwear agents overall, may similarly be as described above for the phosphorus-containing agents, for instance, in certain embodiments 0.05 to 1 percent by weight.

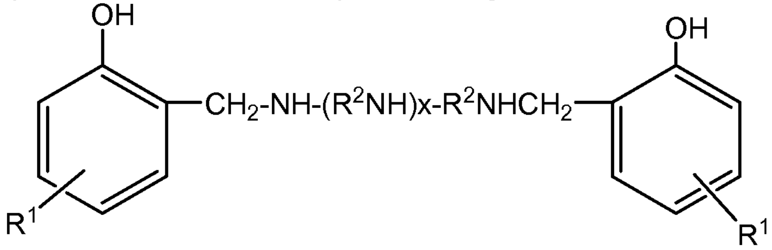
[0069] Dispersants are well known in the field of lubricants and include primarily what is known as ashless-type dispersants and polymeric dispersants. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include nitrogen-containing dispersants such as N-substituted long chain alkenyl succinimides, having a variety of chemical structures including typically



where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight of 500-5000, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892.

[0070] Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0071] Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials may have the general structure



(including a variety of isomers and the like) and are described in more detail in U.S. Patent 3,634,515.

[0072] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0073] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403.

[0074] The amount of dispersant in the present composition can typically be 1 to 10 weight percent, or 1.5 to 9.0 percent, or 2.0 to 8.0 percent, all expressed on an oil-free basis.

[0075] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the compositions of this invention. Viscosity improvers are usually polymers, including polyisobutenes, polymethacrylic acid esters, diene polymers, polyalkyl styrenes, esterified styrene-maleic anhydride copolymers, alkenylarene-conjugated diene copolymers and polyolefins. Multifunctional viscosity improvers, other than those of the present invention, which also have dispersant and/or antioxidancy properties are known and may optionally be used in addition to the products of this invention.

[0076] Other additives that may optionally be used in the lubricating oils of this invention include pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers and anti-foam agents.

[0077] Extreme pressure agents and corrosion and oxidation inhibiting agents which may be included in the compositions of the invention are exemplified by chlorinated aliphatic hydrocarbons, organic sulfides and polysulfides, phosphorus esters including dihydrocarbon and trihydrocarbon phosphites, and molybdenum compounds.

[0078] The various additives described herein can be added directly to the lubricant. In one embodiment, however, they can be diluted with a concentrate-forming amount of a substantially inert, normally liquid organic diluent such as mineral oil or a synthetic oil such as a polyalphaolefin to form an additive concentrate. These concentrates usually comprise 0.1 to 80% by weight of the compositions of this invention and may contain, in addition, one or more other additives known in the art or described hereinabove. Concentrations such as 15%, 20%, 30% or 50% of the additives or higher may be employed. By a "concentrate forming amount" is generally mean an amount of oil or other solvent less than the amount present in a fully formulated lubricant, e.g., less than 85% or 80% or 70% or 60%. Additive concentrates can be prepared by mixing together the desired components, often at elevated temperatures, usually up to 150° C or 130° C or 115° C.

[0079] The lubricating compositions of the present invention may thus impart protection against deterioration in one or more of the properties of engine performance, engine wear, engine cleanliness, deposit control, filterability, and oxidation of engine oils, when they are used to lubricate a surface of a mechanical device such as an engine drive train, for instance, the moving parts of a drive train in a vehicle including an internal surface a component of an internal combustion engine. Such a surface may then be said to contain a coating of the lubricant composition.

[0080] The internal combustion engines to be lubricated may include gasoline fueled engines, spark ignited engines, diesel engines, compression ignited engines, two-stroke cycle engines, four-stroke cycle engines, sump-lubricated engines, fuel-lubricated engines, natural gas-fueled engines, marine diesel engines, and stationary engines. The vehicles in which such engines may be employed include automobiles, trucks, off-road vehicles, marine vehicles, motorcycles, all-terrain vehicles, and snowmobiles. In one embodiment, the lubricated engine is a heavy duty diesel engine, which may include sump-lubricated, two- or four-stroke cycle engines, which are well known to those skilled in the art. Such engines may have an engine displacement of greater than 3, greater than 5, or greater than 7 L.

[0081] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0082] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0083] Formulation A. A formulation is prepared to evaluate the effect of titanium in the presence of borate ester. The formulation contains, in mineral oil, the following additives (each containing the commercially conventional amounts of diluent oil):

10.7% succinimide dispersants
3.98% overbased calcium salixarate, sulfonate, and phenate detergent
2% viscosity modifier
1.81% mixed antioxidants
1.1% zinc dialkyldithiophosphate
0.2% pour point depressant
0.02% corrosion inhibitor
0.01% antifoam agent

plus the amounts of titanium isopropoxide and borate ester (tri-(2-ethylhexyl)borate) as indicated in the table below.

[0084] The samples are subjected to a test of air oxidation by pressure differential scanning calorimetry (PDSC), using industry standard test CECL85 for oxidation induction time. In this test, a sample is measured into a cell which is pressurized with air to 690 kPa (100 psi) and maintained at 210 °C until an oxidation event is detected by heat flow. The oxidation induction time, in minutes, is reported. Longer times are better.

Example	1*	2*	3	4
Alkyl borate, % (ppm B)	0.13 (35)	0.26 (70)	0.13 (35)	0.26 (70)
Ti isopropoxide, % (ppm Ti)	0 (0)	0 (0)	0.048 (81)	0.064 (108)
Oxidation induction time	107.2	109.3	128.4	148.7

* A comparative example

[0085] The results show that the presence of titanium leads to an improvement in oxidative stability. The improvement is significantly better in the presence of borate ester, about 70 ppm B and above, an improvement which is not observed in the absence of the Ti.

[0086] A matrix study further shows the advantages of combinations of titanium and boron on the oxidation induction time. The base formulation is as shown for Examples 1-4; the titanium compound and boron compound are also as in the above examples. The amount of aminic antioxidant is varied, and the relative amounts of high and low TBN phenate detergents are also varied. This study is represented in the following Table:

	Boron	Titanium	Aminic antiox.	Ca phenate A	Ca phenate B	PDSC (OIT)
Ex.	ppm	ppm	% wt.	% wt.	% wt.	min
5	70	100	1.06	0.74	0.3	181.1
6	35	0	1.06	0.74	0.3	104.8
7	35	100	1.06	0.15	1.35	173.6
8	70	0	1.06	0.15	1.35	144.7
9	35	100	0.53	0.74	0.3	134.4
10	70	0	0.53	0.74	0.3	109.3
11	70	100	0.53	0.15	1.35	148.7
12	35	0	0.53	0.15	1.35	110.1
13	35	25	1.06	0.74	0.3	132.1
14	35	25	0.53	0.74	0.3	109.5
15	35	75	1.06	0.74	0.3	172.8
16	38	75	0.53	0.74	0.3	128.4
17	70	25	1.06	0.74	0.3	135.3
18	70	25	0.53	0.74	0.3	124.1
19	70	75	1.06	0.74	0.3	179.3
20	70	75	0.53	0.74	0.3	133.8
21	35	50	1.06	0.74	0.3	157.5
22	35	50	0.53	0.74	0.3	123.4
23	70	50	1.06	0.74	0.3	168.8
24	70	50	0.53	0.74	0.3	132.3
25	52.5	50	0.795	0.74	0.3	143.7
26	52.5	50	0.795	0.74	0.3	135.8
27	105	75	1.06	0.74	0.3	189.5
28	105	25	0.53	0.74	0.3	125.4

Ca phenate A: a calcium alkylphenate sulfide detergent, 255 TBN (39% oil)
Ca phenate B: a calcium alkylphenate sulfide detergent, 145 TBN (27% oil)
Aminic antiox.: nonylated diphenylamines, antioxidant

[0087] The results show that fluids with a high boron level (e.g., 52.5 ppm and above or especially 70 ppm and above or especially 105 ppm and above) and a high titanium level (e.g., 50 ppm and above or especially 75 ppm and above or especially 100 ppm and above) typically show significantly improved PDSC oxidation induction times.

[0088] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

What is claimed is:

1. A method for lubricating an internal combustion engine, comprising supplying to said engine a lubricating composition comprising:

(a) an oil of lubricating viscosity;

(b) at least about 25 parts per million by weight of titanium in the form of an oil-soluble titanium-containing material;

(c) an antioxidant other than a Ti-containing antioxidant,

(d) a metal containing detergent other than a Ti-containing detergent, and

(e) at least about 70 parts per million by weight of boron in the form of a soluble boron compound.

2. The method of claim 1 wherein the soluble boron compound is a borate ester.

3. The method of claim 1or claim 2 wherein said metal-containing detergent of (d) comprises a detergent containing a salicylate moiety.

4. The method of any of claims 1 through 3 wherein the oil-soluble titanium-containing material comprises a titanium alkoxide.

5. The method of any of claims 1 through 3 wherein the oil-soluble titanium-containing material is selected from the group consisting of titanium-modified dispersants, tolyltriazole oligomers salted with or chelated to titanium, titanium citrate, titanium compounds derived from glycols, each of the forego-ing having a number average molecular weight of less than 20,000, and surface-modified TiO_2 nanoparticles

6. The method of any of claims 1 through 3 or claim 5 wherein the oil-soluble titanium-containing material comprises a titanium-modified succinimide dispersant which is the reaction product of a titanium alkoxide and a hydrocarbyl-substituted succinimide dispersant.

7. The method of any of claims 1 through 6 wherein the composition contains less than about 150 parts per million by weight of molybdenum and less than about 1200 parts per million by weight of phosphorus.

8. The method of any of claims 2 through 7 wherein the borate ester comprises the product of boric acid with 2-ethylhexanol.

9. The method of any of claims 1 through 8 wherein the amount of titanium is about 75 to about 1000 parts per million.

10. The method of any of claims 1 through 9 wherein the amount of boron is about 70 to about 1000 parts per million.

11. The method of any of claims 1 through 10 wherein the amount of titanium is about 85 to about 150 parts per million and the amount of boron is about 85 to about 150 parts per million.

12. A lubricating composition comprising:

(a) an oil of lubricating viscosity;

(b) at least about 25 parts per million by weight of titanium in the form of an oil-soluble titanium-containing material;

(c) an antioxidant other than a Ti-containing antioxidant,

(d) a metal containing detergent other than a Ti-containing detergent, and

(e) at least about 70 parts per million by weight of boron in the form of a soluble boron compound.

13. The composition of claim 11 wherein the soluble boron compound is a borate ester.

14. A composition prepared by combining the components of claim 12 or claim 13

15. The composition of any of claims 12 through 14 wherein said metal-containing detergent of (d) comprises a detergent containing a salicylate moiety.

16. The composition of any of claims 12 through 15 wherein the oil-soluble titanium-containing material comprises a titanium alkoxide.

17. The composition of any of claims 12 through 15 wherein the oil-soluble titanium-containing material comprises a titanium-modified succinimide dispersant which is the reaction product of a titanium alkoxide and a hydrocarbyl-substituted succinimide dispersant.

18. The composition of any of claims 12 through 17 wherein the composition contains less than about 150 parts per million by weight of molybdenum and less than about 1200 parts per million by weight of phosphorus.

19. The composition of any of claims 12 through 18 wherein the borate ester comprises the product of boric acid with 2-ethylhexanol.

20. The composition of any of claims 12 through 19 wherein the amount of titanium is about 75 to about 1000 parts per million.

21. The composition of any of claims 12 through 20 wherein the amount of boron is about 70 to about 1000 parts per million

22. The composition of any of claims 12 through 21 wherein the amount of titanium is about 85 to about 150 parts per million and the amount of boron is about 85 to about 150 parts per million.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/077371

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M163/00

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)
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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006/105022 A (LUBRIZOL CORP [US]; BROWN JASON R [US]; ADAMS PAUL E [US]; CARRICK VIR) 5 October 2006 (2006-10-05) paragraphs [0002], [0010] - [0015], [0032], [0036], [0059] - [0064]; claims 1-15; examples 1-19	1-22
X	US 2007/132274 A1 (LAM WILLIAM Y [US] ET AL) 14 June 2007 (2007-06-14) paragraph [0003]; claims 1-5,19; table 2	1,3,7,9, 10,12, 14,15, 18,20,21

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

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"&" document member of the same patent family

Date of the actual completion of the international search 10 December 2008	Date of mailing of the international search report 30/12/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pöllmann, Klaus

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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