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(54) **Lubricating oil composition**

(57) A low SAPS lubricating oil composition exhibiting having up to 0.3 wt.% sulfur, up to 0.08 wt.% phosphorus, and a sulfated ash content up to 0.80 wt.% com-

prising a nitrogen-containing ashless dispersant, a boron source, the wt.% N to wt.% B ratio being 3:1 to 5:1.

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Description

[0001] The present invention relates to lubricating oil compositions. More particularly, the present invention relates to lubricating oil compositions, which have low levels of phosphorus, sulfur and sulfated ash.

BACKGROUND OF THE INVENTION

[0002] Environmental concerns have led to continued efforts to reduce the CO, hydrocarbon and nitrogen oxide (NO_x) emissions of compression ignited (diesel-fueled) and spark ignited (gasoline-fueled) light duty internal combustion engines. Further, there have been continued efforts to reduce the particulate emissions of compression ignited light duty internal combustion engines. To meet the upcoming emission standards for passenger cars, original equipment manufacturers (OEMs) will rely on the use of additional exhaust gas after-treatment devices. Such exhaust gas after-treatment devices may include catalytic converters, which can contain one or more oxidation catalysts, NO_x storage catalysts, and/or NH₃ reduction catalysts; and/or a particulate trap.

[0003] Oxidation catalysts can become poisoned and rendered less effective by exposure to certain elements/compounds present in engine exhaust gasses, particularly by exposure to phosphorus and phosphorus compounds introduced into the exhaust gas by the degradation of phosphorus-containing lubricating oil additives. Reduction catalysts are sensitive to sulfur and sulfur compounds in the engine exhaust gas introduced by the degradation of both the base oil used to blend the lubricant, and sulfur-containing lubricating oil additives. Particulate traps can become blocked by metallic ash, which is a product of degraded metal-containing lubricating oil additives.

[0004] One of the most effective antioxidant and antiwear agents, from both a performance and cost-effectiveness standpoint, used conventionally in lubricating oil compositions for internal combustion engines comprises dihydrocarbyl dithiophosphate metal salts. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. Of these, zinc salts of dihydrocarbyl dithiophosphate (ZDDP) are most commonly used. While such compounds are particularly effective antioxidants and antiwear agents such compounds introduce phosphorus, sulfur and ash into the engine that can shorten the service life of exhaust gas after-treatment devices, as described supra.

[0005] To insure a long service life, lubricating oil additives that exert a minimum negative impact on such after-treatment devices must be identified, and OEM specifications for "new service fill" and "first fill" lubricants are expected to require maximum sulfur levels of 0.30 wt. %; maximum phosphorus levels of 0.08 wt. %, and sulfated ash contents below 0.80 wt. %. Such lubricating oil compositions can be referred to as "low SAPS" (low sulfated ash, phosphorus, sulfur) lubricating oil compositions.

[0006] At the same time, the selected lubricating oil composition must provide adequate lubricant performance, including adequate wear protection and detergency. The performance of lubricating oil compositions used in light duty spark and compression-ignited vehicular internal combustion engines, specifically antiwear and engine cleaning performance, must be maintained at the high level dictated by the "new service", and "first fill" specifications of the OEM's.

SUMMARY OF THE INVENTION

[0007] In accordance with the present invention there is provided a lubricating oil composition having a sulfur content of up to 0.3 wt.%, a phosphorus content of up to 0.08 wt.%, a sulfated ash content of up to 0.80 wt.% which comprises an admixture of :

- (a) a major amount of an oil of lubricating viscosity selected from one or more of the group consisting of Group I, Group II, Group III, Group IV and synthetic ester base stock oils,
- (b) an overbased metal lubricating oil detergent,
- (c) at least one nitrogen-containing dispersant, the dispersant providing to the oil a nitrogen content of at least 0.075 wt. % nitrogen, the dispersant having a polyalkenyl backbone which has a molecular weight range of 900 to 3000 ,
- (d) an oil soluble or oil dispersible source of boron, present in an amount so as to provide a ratio of wt.% nitrogen to wt.% boron in the oil composition of 3:1 to 5:1,
- (e) an antioxidant, and
- (f) a zinc dihydrocarbyldithiophosphate.

[0008] Unless otherwise stated, all amounts of additives are reported in wt. % on an active ingredient ("a.i.") basis, i.e., independent of the diluent or carrier oil.

Oil of Lubricating Viscosity

[0009] The oil of lubricating viscosity may be selected from Group I, II, III or IV base stocks, synthetic ester base stocks or mixtures thereof. The base stock groups are defined in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. The base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8 mm²/s (cSt.) at 100°C.

(a) Group I mineral oil base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120, measured using the test methods specified in Table A below.

(b) Group II mineral oil base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table A below.

(c) Group III mineral oil base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table A below.

(d) Group IV base stocks are polyalphaolefins (PAO).

(e) Suitable ester base stocks that can be used comprise the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(e-ethylhexyl) sebacate, din-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0010] Esters useful as synthetic base stock oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

Table A - Analytical Methods for Testing Base Stocks

Property	Test Method
Saturates	ASTM D2007
Viscosity Index	ASTM D2270
Sulfur	ASTM D2622, D4294, D4927, or D3120

[0011] Preferably, the oil of lubricating viscosity comprises substantially no Group I base stock oil.

[0012] The oil of lubricating viscosity used in this invention should have a viscosity index of at least 95, preferably at least 100. Preferred oils are (a) base oil blends of Group III base stocks with Group II base stocks, where the combination has a viscosity index of at least 110; or (b) Group III base stocks or blends of more than one Group III base stock. Mineral oils are preferred.

Dispersant

[0013] Dispersants useful in the context of the present invention include the range of nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. The ashless, dispersants useful for the present invention suitably comprise an oil soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, such dispersants have amine, amine-alcohol or amide polar moieties attached to the polymer backbone, often via a bridging group. A suitable 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 polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0014] The dispersant of the present invention preferably comprises at least one dispersant that is derived from polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester, which dispersant has a polyalkenyl moiety with

a number average molecular weight of at least 900 and from greater than 1.3 to 1.7, preferably from greater than 1.3 to 1.6, most preferably from greater than 1.3 to 1.5 functional groups (mono- or dicarboxylic acid producing moieties) per polyalkenyl moiety (a medium functionality dispersant). Functionality (F) can be determined according to the following formula:

$$F = (\text{SAP} \times M_n) / ((112,200 \times \text{A.I.}) - (\text{SAP} \times 98)) \quad (1)$$

wherein SAP is the saponification number (i.e., the number of milligrams of KOH consumed in the complete neutralization of the acid groups in one gram of the succinic-containing reaction product, as determined according to ASTM D94); M_n is the number average molecular weight of the starting olefin polymer; and A.I. is the percent active ingredient of the succinic-containing reaction product (the remainder being unreacted olefin polymer, succinic anhydride and diluent).

[0015] Generally, each mono- or dicarboxylic acid-producing moiety will react with a nucleophilic group (amine, alcohol, amide or ester polar moieties) and the number of functional groups in the polyalkenyl-substituted carboxylic acylating agent will determine the number of nucleophilic groups in the finished dispersant.

[0016] The polyalkenyl moiety of the dispersant of the present invention has a number average molecular weight of at least 900, suitably at least 1500, preferably between 1800 and 3000, such as between 2000 and 2800, more preferably from 2100 to 2500, and most preferably from 2200 to 2400. The molecular weight of a dispersant is generally expressed in terms of the molecular weight of the polyalkenyl moiety as the precise molecular weight range of the dispersant depends on numerous parameters including the type of polymer used to derive the dispersant, the number of functional groups, and the type of nucleophilic group employed.

[0017] 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 for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

[0018] The polyalkenyl moiety suitable for forming the dispersant used in the dispersant composition of the present invention preferably has a narrow molecular weight distribution (MWD), also referred to as polydispersity, as determined by the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n). Polymers having a M_w/M_n of less than 2.2, preferably less than 2.0, are most desirable. Suitable polymers have a polydispersity of from 1.5 to 2.1, preferably from 1.6 to 1.8.

[0019] Suitable hydrocarbons or polymers employed in the formation of the dispersants of the present invention include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C_3 to C_{28} alpha-olefin having the formula $H_2C=CHR^1$ wherein R^1 is straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, preferably a high degree of terminal ethenylidene unsaturation. Preferably, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R^1 is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms.

[0020] Another useful class of polymers is polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common polymers from this class include polyisobutenes obtained by polymerization of a C_4 refinery stream having a butene content of 35 to 75% by wt., and an isobutene content of 30 to 60% by wt., in the presence of a Lewis acid catalyst, such as aluminum trichloride or boron trifluoride. A preferred source of monomer for making poly-n-butenes is petroleum feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. Polyisobutylene is a most preferred backbone of the present invention because it is readily available by cationic polymerization from butene streams (e.g., using $AlCl_3$ or BF_3 catalysts). Such polyisobutylenes generally contain residual unsaturation in amounts of one ethylenic double bond per polymer chain, positioned along the chain. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Preferably, these polymers, referred to as highly reactive polyisobutylene (HR-PIB), have a terminal vinylidene content of at least 65%, e.g., 70%, more preferably at least 80%, most preferably, at least 85%. The preparation of such polymers is described, for example, in U.S. Patent No. 4,152,499. HR-PIB is known and HR-PIB is commercially available under the tradenames Glissopal™ (from BASF) and Ultravis™ (from BP-Amoco).

[0021] Polyisobutylene polymers that may be employed are generally based on a hydrocarbon chain of from 1500 to 3000. Methods for making polyisobutylene are known. Polyisobutylene can be functionalized by halogenation (e.g. chlorination), the thermal "ene" reaction, or by free radical grafting using a catalyst (e.g. peroxide), as described below.

[0022] The hydrocarbon or polymer backbone can be functionalized, e.g., with carboxylic acid producing moieties (preferably acid or anhydride moieties) selectively at sites of carbon-to-carbon unsaturation on the polymer or hydrocarbon chains, or randomly along chains using any of the three processes mentioned above or combinations thereof, in any sequence.

[0023] Processes for reacting polymeric hydrocarbons with unsaturated carboxylic acids, anhydrides or esters and the preparation of derivatives from such compounds are disclosed in U.S. Patent Nos. 3,087,936; 3,172,892; 3,215,707; 3,231,587; 3,272,746; 3,275,554; 3,381,022; 3,442,808; 3,565,804; 3,912,764; 4,110,349; 4,234,435; 5,777,025; 5,891,953; as well as EP 0 382 450 B1; CA-1,335,895 and GB-A-1,440,219. The polymer or hydrocarbon may be functionalized, for example, with carboxylic acid producing moieties (preferably acid or anhydride) by reacting the polymer or hydrocarbon under conditions that result in the addition of functional moieties or agents, i.e., acid, anhydride, ester moieties, etc., onto the polymer or hydrocarbon chains primarily at sites of carbon-to-carbon unsaturation (also referred to as ethylenic or olefinic unsaturation) using the halogen assisted functionalization (e.g. chlorination) process or the thermal "ene" reaction.

[0024] Selective functionalization can be accomplished by halogenating, e.g., chlorinating or brominating the unsaturated α -olefin polymer to 1 to 8 wt. %, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer or hydrocarbon, by passing the chlorine or bromine through the polymer at a temperature of 60 to 250°C, preferably 110 to 160°C, e.g., 120 to 140°C, for 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer or hydrocarbon (hereinafter backbone) is then reacted with sufficient monounsaturated reactant capable of adding the required number of functional moieties to the backbone, e.g., monounsaturated carboxylic reactant, at 100 to 250°C, usually 180°C to 235°C, for 0.5 to 10, e.g., 3 to 8 hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated backbones. Alternatively, the backbone and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material.

[0025] The hydrocarbon or polymer backbone can be functionalized by random attachment of functional moieties along the polymer chains by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of 100 to 260°C, preferably 120 to 240°C. Preferably, free-radical initiated grafting would be accomplished in a mineral lubricating oil solution containing, e.g., 1 to 50 wt.%, preferably 5 to 30 wt. % polymer based on the initial total oil solution.

[0026] The preferred monounsaturated reactants that are used to functionalize the backbone comprise mono- and dicarboxylic acid material, i.e., acid, anhydride, or acid ester material, including (i) monounsaturated C_4 to C_{10} dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or diesters of (i); (iii) monounsaturated C_3 to C_{10} monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, i.e., of the structure $-C=C-CO-$; and (iv) derivatives of (iii) such as C_1 to C_5 alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i) - (iv) also may be used. Upon reaction with the backbone, the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C_1 to C_4 alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate.

[0027] To provide the required functionality, the monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from equimolar amount to 100 wt. % excess, preferably 5 to 50 wt. % excess, based on the moles of polymer or hydrocarbon. Unreacted excess monounsaturated carboxylic reactant can be removed from the final dispersant product by, for example, stripping, usually under vacuum, if required.

[0028] The functionalized oil-soluble polymeric hydrocarbon backbone is then 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., polyalkene and polyoxyalkylene polyamines of 2 to 60, such as 2 to 40 (e.g., 3 to 20) total carbon atoms having 1 to 12, such as 3 to 12, preferably 3 to 9, most preferably from 6 to 7 nitrogen atoms per 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, for example, 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. Such polyamine mixtures, known as PAM, are commercially available. Particularly preferred polyamine mixtures

are mixtures derived by distilling the light ends from PAM products. The resulting mixtures, known as "heavy" PAM, or HPAM, are also commercially available. The properties and attributes of both PAM and/or HPAM are described, for example, in U.S. Patent Nos. 4,938,881; 4,927,551; 5,230,714; 5,241,003; 5,565,128; 5,756,431; 5,792,730; and 5,854,186.

[0029] Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane and heterocyclic nitrogen compounds such as imidazolines. Another useful class of amines is the polyamido and related amido-amines as disclosed in U.S. Patent Nos. 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (TAM) as described in U.S. Patent Nos. 4,102,798; 4,113,639; 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structured amines may also be used. Similarly, one may use condensed amines, as described in U.S. Patent No. 5,053,152. The functionalized polymer is reacted with the amine compound using conventional techniques as described, for example, in U.S. Patent Nos. 4,234,435 and 5,229,022, as well as in EP-A-208,560.

[0030] The functionalized, oil-soluble polymeric hydrocarbon backbones may also be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols, or with aromatic compounds such as phenols and naphthols. Preferred polyhydric alcohols include 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 alcohols capable of yielding ashless dispersants comprise ether-alcohols, including oxy-alkylene and oxyarylene. Such ether-alcohols 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 acid-esters, i.e., partially esterified succinic acids, as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxy radicals. An ester dispersant may be prepared by any one of several known methods as described, for example, in U.S. Patent No. 3,381,022.

[0031] Another class of high molecular weight ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing one mole of a long chain alkyl-substituted mono- or polyhydroxy benzene with 1 to 2.5 moles of carbonyl compound(s) (e.g., formaldehyde and paraformaldehyde) and 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Patent No. 3,442,808. Such Mannich base condensation products may include a polymer product of a metallocene catalyzed polymerization 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 described in U.S. Patent No. 3,442,808. Examples of functionalized and/or derivatized olefin polymers synthesized using metallocene catalyst systems are described in the publications identified *supra*.

[0032] The dispersant(s) of the invention are preferably non-polymeric (e.g., are mono- or bis-succinimides).

[0033] The dispersant(s) of the present invention can be borated by conventional means, as generally taught in U.S. Patent Nos. 3,087,936, 3,254,025 and 5,430,105. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from 0.1 to 20 atomic proportions of boron for each mole of acylated nitrogen composition.

[0034] The boron, which appears in the product as dehydrated boric acid polymers (primarily $(\text{HBO}_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of the diimide. Boration can be carried out by adding a sufficient quantity of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135°C to 190°C, e.g., 140°C to 170°C, for from 1 to 5 hours, followed by nitrogen stripping. Alternatively, the boron treatment can be conducted by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine, while removing water. Other post reaction processes known in the art can also be applied.

[0035] The lubricating oil composition of the present invention has a ratio of wt. % nitrogen to wt. % boron of from 3:1 to 5:1. In an embodiment of the present invention, the lubricating oil composition may have a ratio of wt % nitrogen to wt % boron of from 3:1 to 4.5:1. The boron source may be boron provided by using a borated dispersant, but may also be provided by a separately added oil soluble or oil dispersible boron compound, including another dispersant.

Oil Soluble or Oil Dispersible Boron Compound

[0036] The source of boron for the compositions of this invention may be provided by borating the nitrogen containing dispersant so as to provide the appropriate amount of boron or the boron may be added to the lubricating oil composition by means of a separate oil dispersible or oil soluble boron compound, which may be another dispersant, and such a boron containing additional dispersant will preferably be a borated polyisobutenyl succinimide where the polyisobutenyl may have a broad molecular weight range, such as Mn 450 to 3000.

[0037] Non-dispersant boron sources are prepared by reacting a boron compound with an oil-soluble or oil-dispersible

additive or compound. Boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. Suitable "non-dispersant boron sources" may comprise any oil-soluble, boron-containing compound, but preferably comprise one or more boron-containing additives known to impart enhanced properties to lubricating oil compositions. Such boron-containing additives include, for example, borated dispersant VI improver; alkali metal, mixed alkali metal or alkaline earth metal borate; borated overbased metal detergent; borated epoxide; borate ester; and borate amide.

[0038] Alkali metal and alkaline earth metal borates are generally hydrated particulate metal borates, which are known in the art. Alkali metal borates include mixed alkali and alkaline earth metal borates. These metal borates are available commercially. Representative patents describing suitable alkali metal and alkaline earth metal borates and their methods of manufacture include U.S. Patent Nos. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790.

[0039] The borated amines may be prepared by reacting one or more of the above boron compounds with one or more of fatty amines, e.g., an amine having from four to eighteen carbon atoms. They may be prepared by reacting the amine with the boron compound at a temperature of from 50 to 300, preferably from 100 to 250 °C and at a ratio from 3:1 to 1:3 equivalents of amine to equivalents of boron compound.

[0040] Borated fatty epoxides are generally the reaction product of one or more of the above boron compounds with at least one epoxide. The epoxide is generally an aliphatic epoxide having from 8 to 30, preferably from 10 to 24, more preferably from 12 to 20, carbon atoms. Examples of useful aliphatic epoxides include heptyl epoxide and octyl epoxide. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from 14 to 16 carbon atoms and from 14 to 18 carbon atoms. The borated fatty epoxides are generally known and are described in U.S. Patent 4,584,115.

[0041] Borate esters may be prepared by reacting one or more of the above boron compounds with one or more alcohol of suitable oleophilicity. Typically, the alcohol contains from 6 to 30, or from 8 to 24, carbon atoms. Methods of making such borate esters are known in the art.

[0042] The borate esters can be borated phospholipids. Such compounds, and processes for making such compounds, are described in EP-A-0 684 298.

[0043] Borated overbased metal detergents are known in the art where the borate substitutes the carbonate in the core either in part or in full.

Metal Detergent

[0044] The present invention requires the presence of an overbased metal-containing lubricating oil detergent having a TBN of 150 to 450. These metal detergents may be present in such amounts to provide their normal attendant functions so long as the sulfated ash content of the oil remains at 0.80 wt. % or less, and generally are used in amounts of from 0.5 to 3 wt. %.

[0045] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with long hydrophobic tail, with the polar head comprising a metal salt of an acid organic compound. The salts may contain a substantially stoichiometric amount of the metal in which they are usually described as normal or neutral salts, and would typically have a total base number (TBN), as may be measured by ASTM D-2896 of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acid gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and overbased detergents typically used have a TBN from 250 to 450, or more.

[0046] Detergents that are conventionally employed include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Combinations of detergents, whether overbased or neutral or both, may be used.

[0047] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. The alkaryl sulfonates usually contain from 9 to 80 or more carbon atoms, preferably from 16 to 60 carbon atoms per alkyl substituted aromatic moiety.

[0048] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or

more phenols are bridged by sulfur containing bridges.

[0049] Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges.

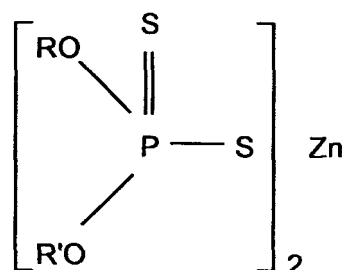
[0050] Preferred substituents in oil-soluble salicylic acids are alkyl substituents. In alkyl - substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility. Calcium alkyl salicylate detergents are preferred for use in the present invention.

Antioxidants

[0051] Antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. They are generally present in amount of from 0.1 to 5.0 wt.%, preferably 0.25 to 1.0 wt.%. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, alkyl substituted diphenylamine, alkyl substituted phenyl and naphthylamines, phosphorous esters, metal thiocarbamates, ashless thiocarbamates and oil soluble copper compounds as described in U.S. 4,867,890. Most preferred are the dialkyl substituted diphenylamines, wherein the alkyl is C₄-C₂₀, such as dinonyl diphenylamine and the hindered phenols, such as isooctyl-3,5-di-tert-butyl-4-hydroxycinnamate and mixtures of same.

Zinc Dihydrocarbyldithiophosphates

[0052] The zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be 5 or greater. The zinc dihydrocarbyl dithiophosphate (ZDDP) can therefore comprise zinc dialkyl dithiophosphates. ZDDP is the most commonly used antioxidant/antiwear agent in lubricating oil compositions for internal combustion engines, and in conventional passenger car diesel engines formulated to meet present European ACEA specifications. The lubricating oil compositions of the present invention suitably contain an amount of ZDDP (or other dihydrocarbyl dithiophosphate metal salt) that introduces 0.02 to 0.08 wt.%, preferably 0.02 to 0.06 wt.% of phosphorus into the lubricating oil composition. The phosphorus content of the lubricating oil compositions is determined in accordance with the procedures of ASTM D5185.

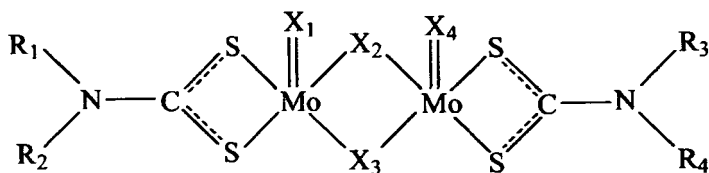
[0053] Preferred, optional ingredients, further include oil soluble organomolybdenum compounds, friction modifiers, and viscosity modifiers.

Molybdenum Compound

[0054] For the lubricating oil compositions of this invention, any suitable oil soluble organo-molybdenum compound

may be employed. The molybdenum compound will function both as an antiwear and antioxidant additive. Preferably, dimeric and trimeric molybdenum compounds are used. Examples of such oil soluble organo-molybdenum compounds are the dialkyldithiocarbamates, dialkyldithiophosphates, dialkyldithiophosphinates, xanthates, thioxanthates, carboxylates and the like, and mixtures thereof. Particularly preferred are molybdenum dialkyldithiocarbamates.

[0055] The molybdenum dialkyldithiocarbamate dimer to be used as an additive in the present invention is a compound expressed by the following formula:

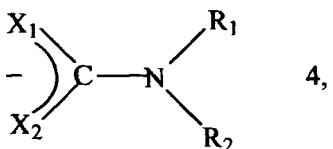
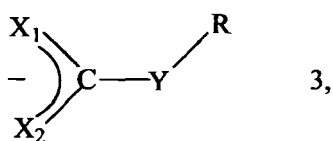
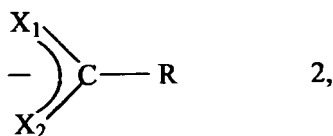


R_1 through R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group; and X_1 through X_4 independently denote an oxygen atom or a sulfur atom. The four hydrocarbyl groups, R_1 through R_4 , may be identical or different from one another.

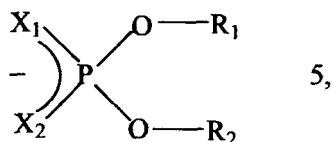
[0056] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear (trimeric) molybdenum compounds, especially those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble in the oil, n is from 1 to 4, k varies from 4 to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0057] The ligands are selected from the group consisting of

-X-R 1,



and



and mixtures thereof, wherein X, X₁, X₂, and Y are independently selected from the group of oxygen and sulfur, and wherein R₁, R₂, and R are independently selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. More preferably, each ligand has the same hydrocarbyl group.

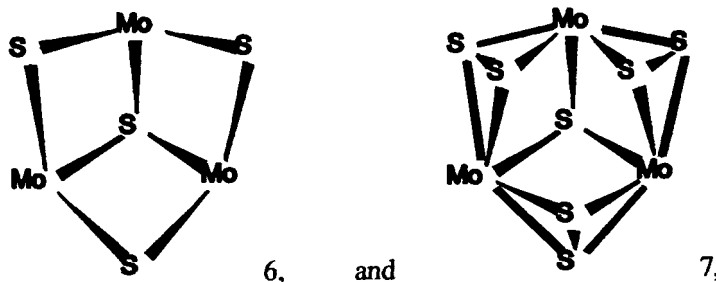
[0058] The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following:

1. Hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group).

2. Substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

[0059] Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble in the oil. For example, the number of carbon atoms in each group will generally range between 1 to about 100, preferably from 1 to 30, and more preferably between 4 to 20. Preferred ligands include dialkyldithiophosphate, alkylxanthate, carboxylates, dialkyldithiocarbamate, and mixtures thereof. Most preferred are the dialkyldithiocarbamates. Those skilled in the art will realize that formation of the compounds requires selection of ligands having the appropriate charge to balance the core's charge (as discussed below).

[0060] Compounds having the formula Mo₃S_kL_nQ_z have cationic cores surrounded by anionic ligands, wherein the cationic cores are represented by structures such as



which have net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. Four monoanionic ligands are preferred. Without wishing to be bound by any theory, it is believed that two or more trinuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate, i.e., having multiple connections to one or more cores. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

[0061] Oil-soluble trinuclear molybdenum compounds are preferred and can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source such as (NH₄)₂Mo₃S₁₃·n(H₂O), where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetraalkylthiuram disulfide. Other oil-soluble trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as (NH₄)₂Mo₃S₁₃·n(H₂O), a ligand source such as tetraalkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur abstracting agent such cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear

molybdenum-sulfur halide salt such as $[M']_2[Mo_3S_7A_6]$, where M' is a counter ion, and A is a halogen such as Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

[0062] The ligand chosen must have a sufficient number of carbon atoms to render the compound soluble in the lubricating composition. The term "oil-soluble" as used herein does not necessarily indicate that the compounds or additives are soluble in the oil in all proportions. It does mean that they are soluble in use, transpofiation, and storage.

[0063] A sulfurized molybdenum containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a phosphoramidate, a thiophosphoramidate, a Mannich base, a dispersant viscosity index improver, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex (ii) reacting the molybdenum complex with a sulfur containing compound, to thereby form a sulfur and molybdenum containing composition is useful within the context of this invention. The sulfurized molybdenum containing compositions may be generally characterized as a molybdenum/sulfur complex of a basic nitrogen compound. The precise molecular formula of these molybdenum compositions is not known with certainty. However, they are believed to be compounds in which molybdenum, whose valences are satisfied with atoms of oxygen or sulfur, is either complexed by, or the salt of one or more nitrogen atoms of the basic nitrogen containing compound used in the preparation of these compositions.

[0064] The lubricating compositions of the present invention may contain a minor amount of an oil soluble molybdenum compound. An amount of at least 10 ppm up to 2,000 ppm of molybdenum from a molybdenum compound may be present in the lubricating oil composition. Preferably, 500 ppm to 1,000 ppm of molybdenum from a molybdenum compound is used. These values are based upon the weight of the lubricating composition.

Friction Modifiers

[0065] At least one organic oil soluble friction modifier may preferably be incorporated in the lubricating oil composition. Typically, the friction modifier makes up 0.02 to 2.0 wt.% of the lubricating oil composition. Preferably, from 0.05 to 1.0, more preferably from 0.1 to 0.5 wt.% of the friction modifier is used.

[0066] Friction modifiers include such compounds as aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters of polyols such as glycerol esters of fatty acids as exemplified by glycerol oleate, which is preferred, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

Lubricating Oil Flow Improver

[0067] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like. These may be used in amounts of from 0.01 to 5.0 wt.%, preferably 0.1 to 3.0 wt.%. They are preferably used when mineral oil base stocks are employed but are not required when the base stock is a PAO or synthetic ester.

Viscosity Modifier

[0068] The viscosity modifier (VM) functions to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional. It may be present in amounts of from 0.01 to 20.0 wt.%, preferably 1.0 to 10.0 wt.%. These are preferably employed when the base stock is a mineral oil.

[0069] Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers 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 and isoprene/divinylbenzene.

[0070] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0071] 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 does not require further elaboration.

[0072] The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the

components can be added directly to the base stock or base oil blend by dispersing or dissolving it in the base stock or base oil blend at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature. The invention comprising the product results from the admixture of the additive components to form a lubricating oil composition.

[0073] Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package described herein as the additive package, that is subsequently blended into base stock to make the finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of a base lubricant.

[0074] The concentrate is preferably made in accordance with the method described in U.S. 4,938,880. That patent describes making a pre-mix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least 100°C. Thereafter, the pre-mix is cooled to at least 85°C and the additional components are added.

[0075] The final crankcase lubricating oil formulation may employ from 2 to 20 mass %, preferably 4 to 18 mass %, and most preferably 5 to 17 mass % of the concentrate or additive package, with the remainder being base stock.

[0076] Advantageously, lubricating oil compositions according to the present invention have been found to exhibit a passing value for piston cleanliness and viscosity control in the fired engine XUD-IIBTE test and satisfy the requirements of the Mercedes Benz Seals test despite complying with the low SAPS requirements.

EXAMPLE 1

[0077] The following oil A was prepared and tested for piston merits and viscosity increase according to the XUD-ITBTE fired engine test, a European passenger car diesel engine test (CEC L-56-T-98) which is part of the ACEA B specification.. A higher piston merits value represents a better result than a lower value, and a lower absolute viscosity increase value represents a better result than a higher value. In addition, VW and Mercedes-Benz Seals tests were also carried out. The piston merits and viscosity increase tests of the XUD-IIBTE fired engine test were carried out on comparative Oils B and C. The results are given in Table 1. The VW and Mercedes-Benz Seals tests were carried out on comparative Oils B and C. The results are given in Table 2.

[0078] Oil A shows a distinct and surprising improvement in the XUD-IIBTE and VW and Mercedes-Benz Seals tests.

[0079] Oil A: a lubricating oil composition was prepared containing a calcium alkyl salicylate detergent, 3.02 wt. % non-borated polyisobutenyl (Mn 2300) succinimide dispersant, 0.9 wt% borated polyisobutenyl (Mn 950) succinimide dispersant antioxidant, lubricating oil flow improver, viscosity modifier, antifoam agent, zinc dihydrocarbyl dithiophosphate and mineral oil base stocks. Oil A had a wt.% N to wt. % B ratio of 3.8 to 1, a sulfated ash content of 0.8 wt.%, and had 0.087 wt.% N, 0.24 wt.% S and 0.08 wt.% P.

COMPARATIVE EXAMPLES B and C

[0080] Oil B: the formulation of Oil B above was duplicated except that the borated dispersant was present in an amount of 0.23 wt. %. The oil had a wt.% N to wt. % B ratio of 10 to 1, a sulfated ash content of 0.8 wt.%, and had 0.069 wt.% N, 0.21 wt.% S and 0.08 wt.% P.

[0081] Oil C: the formulation of Oil C above was duplicated except that there was present 3.65 wt. % of the same non-borated dispersant. The oil had a wt.% N to wt. % B ratio of 13 to 1, a sulfated ash content of 0.8 wt.%, and had 0.082 wt.% N, 0.19 wt.% S and 0.08 wt.% P.

TABLE 1

OIL TESTED	OIL A	OIL B	OIL C
Absolute Viscosity Increase @100°C with 3% Soot (CST)	14.9	35.7	29.2
Piston Merit Average	51.7	47.0	53.3

TABLE 2

OIL TESTED	OIL A	OIL C	LIMIT	
VW Seals				
PV3344 Elongation at break ΔK6 (%)	190	175	>160	
PV3344 Tensile strength ΔK6 (MPa)	8.2	7.3	>8	
Mercedes-Benz Seals			Min	Max
NBR34 PCT Elongation at Break	-28	-38	-35	
NBR34 PCT Tensile Strength Change	-6.3	-10	-20	
NBR34 PCT Volume Change	0.4	0.5	0	10
NBR34 PTS Hardness Change	0	1	-8	2

Claims

1. A lubricating oil composition having a sulfur content of up to 0.3 wt.%, a phosphorus content of up to 0.08 wt.%, a

sulfated ash content of up to 0.80 wt.% which comprises an admixture of:

- (a) a major amount of an oil of lubricating viscosity
- (b) at least one nitrogen-containing dispersant, the dispersant providing to the oil a nitrogen content of at least 0.075 wt. % nitrogen, the dispersant having a polyalkenyl backbone which has a molecular weight range of 900 to 3000, and
- (c) an oil soluble or oil dispersible source of boron, present in an amount so as to provide a ratio of wt.% nitrogen to wt.% boron in the oil composition of 3:1 to 5:1.

2. The composition of claim 1, further comprising one or more of a member of the group consisting of an overbased metal containing detergent, an antioxidant, a zinc dihydrocarbyldithiophosphate, oil soluble organomolybdenum compounds, friction modifiers and viscosity modifiers.

3. The composition of claim 2, wherein the detergent is calcium alkyl salicylate of TBN 200 - 400.

4. The composition of claim 1, 2 or 3, wherein the dispersant is a polyisobutenyl succinimide.

5. The composition of any one of the preceding claims, wherein the boron compound is a separately added borated polyisobutenyl succinimide dispersant.

6. The composition of any one of claims 2 to 5, comprising an antioxidant that is (i) a dialkyl diphenylamine wherein the alkyl is C₄-C₂₀ alkyl or (ii) a hindered phenol.

7. The composition of any one of claims 2 to 6, wherein the hydrocarbyl groups of the zinc dihydrocarbyldithiophosphate have 2 to 8 carbon atoms

8. The composition of any one of claims 2 to 7, wherein the organomolybdenum compound is a dialkyldithiocarbamate

9. The composition of any one of the preceding claims, wherein the oil of lubricating viscosity is a mineral oil.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 10 7063

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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Place of search Munich		Date of completion of the search 12 September 2005	Examiner Perakis, N
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 September 2005	Examiner Perakis, N
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03/02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 10 7063

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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