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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number
WO 2004/053033 A1

(51) International Patent Classification⁷: C10M 169/04

(21) International Application Number: PCT/US2003/038385

(22) International Filing Date: 2 December 2003 (02.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/431,306 6 December 2002 (06.12.2002) US

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(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MOLYBDENUM-CONTAINING LUBRICANT FOR IMPROVED POWER OR FUEL ECONOMY

(57) **Abstract:** Lubricant compositions of (a) an oil of lubricating viscosity; (b) a molybdenum salt; (c) a monoester of (i) a polyol and (ii) an aliphatic carboxylic acid containing about 12 to about 24 carbon atoms; and (d) a borate ester of a vicinal diol containing 12 to 24 carbon atoms provide good fuel economy and power output to internal combustion engines.

TITLE

Molybdenum-Containing Lubricant for Improved Power or Fuel Economy

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a lubricant composition for use in internal combustion engines. The lubricants in particular include a molybdenum salt and certain esters and borated esters.

[0002] Lubricating oil compositions containing molybdenum dithiocarbamates are known. U.S. Patent 4,846,983 discloses molybdenum dithiocarbamates derived from a hydrocarbyl primary amine (e.g., oleyl amine), a molybdenum compound (e.g., MoO_3), and carbon disulfide. The reference indicates that these molybdenum dithiocarbamates are useful as antioxidants, anti-wear additives, extreme pressure additives, and friction modifiers in lubricating oil compositions.

[0003] Improved fuel economy and power output are often competing goal in engine and lubricant design. The purpose of this invention is to provide a lubricant which produces the maximum horsepower for a given speed. Consequently, the resulting lubricant will also provide excellent fuel economy characteristics for passenger car motor oils.

SUMMARY OF THE INVENTION

[0004] The present invention relates to a lubricant composition comprising:

(a) an oil of lubricating viscosity;

(b) a molybdenum salt;

(c) a monoester of (i) a polyol and (ii) an aliphatic carboxylic acid containing 12 to 24 carbon atoms; and

(d) a borate ester of a vicinal diol containing 12 to 24 carbon atoms.

[0005] The invention further provided a method for lubricating an internal combustion engine, comprising supplying thereto the above lubricant composition.

DETAILED DESCRIPTION OF THE INVENTION

[0006] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0007] One component of the present invention is an oil of lubricating viscosity. Oils of lubricating viscosity include natural and synthetic lubricating oils and mixtures thereof.

[0008] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0009] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, poly(1-hexenes, poly(1-octenes), poly(1-decenes), and mixtures thereof); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, and di(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, and alkylated polyphenyls), alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs, and homologs thereof.

[0010] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, or similar reaction constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1,000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C3-C8 fatty acid esters, or the C13 Oxo acid diester of tetraethylene glycol.

[0011] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0012] Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.

[0013] Other oils of lubricating viscosity, which may be classified as synthetic oils, are those derived from a gas-to-liquid conversion process, or a Fischer-Tropsch process. Such liquids are made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. The resulting hydrocarbons typically are subjected to further processing, such as hydroisomerization, hydrocracking, or dewaxing.

[0014] Unrefined, refined and rerefined oils (and mixtures of each with each other) of the type disclosed hereinabove can be used in the lubricant compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except that they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those of skill in the art such a solvent extraction, acid or base extraction, filtration, percolation, or similar purification techniques. Rerefined oils are obtained by processes similar to those used to obtain refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0015] Oils of lubricating viscosity have also been characterized by the API as Groups I, II, III, IV, and V, on the basis of sulfur content, amount of saturates, and viscosity index (for Groups I – III), with all polyalphaolefins referred to as Group IV and all others not in Groups I – IV as Group V. Group III oils are often blended with synthetic oils. The present invention can be used in any of these API Groups or blends thereof.

[0016] As an additional component, which is often considered along with the oil of lubricating viscosity as a part of the base stock, is a viscosity index modifier. Viscosity modifiers are commonly used in natural lubricating formulations, and are sometimes unnecessary in high grade synthetic formulations. Viscosity modifiers are generally polymeric materials which are well known to those skilled in the art of lubricant formulation, and include polyisobutenes, polymethacrylate acid esters, polyacrylate acid esters, diene polymers, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins and multifunctional viscosity improvers, including dispersant viscosity modifiers (which impart both dispersancy and viscosity improvement).

[0017] The formulations of the present invention can be used in lubricating oils without particular restriction as to viscosity grade. For instance, they can be used in oils, optionally including a viscosity modifier, having an SAE multigrade viscosity rating of 0W-10, 0W-20, 0W-30, 5W-20, or 5W-30, or in monograde oils having SAE viscosity ratings of 20 or 30.

[0018] When the lubricating oil formulation is used in a synthetic oil base stock, the oil can advantageously be a blend of a polyalphaolefin and a synthetic ester. The polyalphaolefin and the synthetic ester can be present, for example, in weight ratios of 95:5 to 80:20 or about 90:10. These oils can be selected from materials having suitable viscosity to provide to the composition a viscosity grade of 0W-10, with or without the presence of a viscosity modifier. Such a formulation may be desirable for very high performance or racing applications.

[0019] The oil of lubricating viscosity is typically the major component of the lubricant, comprising the balance of the composition after the additives are accounted for. Typically the oil will comprise 50-99 percent by weight of the composition, or 80 to 97 percent, or 85 to 95 percent. When the composition is presented in the form of a concentrate, in which the concentration of the additive or additives is increased by about an order of magnitude, the amount of oil will be correspondingly decreased.

[0020] To the oil of lubricating viscosity is added a molybdenum salt. Particularly useful molybdenum salts include molybdenum dithiocarbamates (or, commonly, molybdenum dihydrocarbyldithiocarbamates, “MoDTC”), which are generally represented by the formula

$$[\ R_1R_2N\text{–}C(=S)S\text{–}]_2\text{–}(Mo_2S_mO_n)$$

where R_1 and R_2 are the same or different groups, including hydrocarbyl groups such as alkyl groups, or hydrogen; typically R_1 and R_2 are C_8 to C_{18} hydrocarbyl groups; m and n are positive integers whose total is 4. Typically m is 1-4 and n is 0-3; preferably m is 2-4 or 2-3 and n is 0-2 or 1-2, respectively. In a particularly preferred material m is 2 and n is 2.

[0021] Specific examples of MoDTCs include commercial materials such as Vanlube™ 822 and Molyvan™ A from R.T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165 and S-600 from Asahi Denka Kogyo K.K. Other molybdenum dithiocarbamates are described by Tomizawa in U.S. Patent 5,688,748; by Ward in U.S. Patent 4,846,983; by deVries et al. in U.S. Patent 4,265,773; and by Inoue et al. in U.S. Patent 4,529,536. Common groups for R_1

and R_2 are 2-ethylhexyl groups and alkyl groups generally containing 6 to 18 carbon atoms, including, in one example, mixtures of alkyl groups containing 6 and 13 carbon atoms.

[0022] R_1 and R_2 can each be independently not only hydrocarbyl groups, but also aminoalkyl groups or acylated aminoalkyl groups. More generally, any such R groups are derived from a basic nitrogen compound (comprising the structure R_1-N-R_2) as described in detail in U.S. Patent 4,265,773. If they are hydrocarbyl groups, they can be alkyl groups of 4 to 24 carbons, typically 6 to 18 carbons, or 8 to 12 carbons. A useful C-8 group is the 2-ethylhexyl group; thus, the di-2-ethylhexyl dithiocarbamate is a preferred group.

[0023] The aminoalkyl groups which can serve as R_1 or R_2 typically arise from the use of a polyalkylenepolyamine in the synthesis of the dithiocarbamate moiety. Typical polyalkenepolyamines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and corresponding higher homologues, and mixtures thereof Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Such polyamines can be prepared by the reaction of ethylene dichloride with ammonia or by reaction of an ethylene imine with a ring opening reagent such as water or ammonia. These reactions result in the production of a complex mixture of polyalkylenepolyamines including cyclic condensation products such as piperazines, which mixtures are also useful. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave as residue what is often termed "polyamine bottoms."

[0024] R_1 and R_2 can be acylated aminoalkane groups, particularly arising from the use of an acylated polyalkylenepolyamine in the synthesis of the dithiocarbamate moiety. Acylated polyalkylenepolyamines typically find use as dispersants for lubricating applications. If a hydrocarbyl diacid such as hydrocarbyl-substituted succinic acid or anhydride is reacted, as the acylating agent, with a polyalkylenepolyamine, the product is typically known as a succinimide dispersant. If a monocarboxylic acid, such as isostearic acid, is used as the acylating agent, the resulting product will typically be an amide, although cyclization to form an imidazoline structure can also occur.

[0025] In this instance, the molybdenum salt can be described as the product of (a) reacting a carboxylic acid or reactive equivalent thereof having, for example, 8 to 34 carbon atoms with an alkylene polyamine; and (b) reacting the product of (a) with, in any order, (i) a molybdenum compound such as MoO_3, H_2MoO_4, Mo $(CO)_6$, $Mo(OH)_3$, MoS_2, or phosphomolybdic acid, and (ii) carbon disulfide, thereby forming a molybdenum dithiocarbamate.

[0026] All such materials are well known to those skilled in the art. Succinimide dispersants and their synthesis are disclosed, for instance, in U.S. Patent 4,234,435. Imidazolines are disclosed in U.S. Patent 2,466,517.

[0027] The preparation of molybdenum thiocarbamates from the above basic nitrogen compounds is described in greater detail in U.S. Patent 4,265,773. In brief, they are conventionally prepared by the reaction of an acidic molybdenum compound such as molybdic acid (or any of the above-mentioned Mo compounds), with the basic nitrogen compound, and subsequent reaction with carbon disulfide.

Example A

[0028] Polyethyleneamine bottoms (1.31 kg, 31.7 equivalents) are charged to a 12 L flask equipped with a Dean-Stark distillate trap, stirrer, thermal probe, and subsurface N_2 sparge set to 8.5 L/hr (0.3 std. cubic feet per hour) and heated to 75-85°C. Isostearic acid (5.92 kg, 19.4 equivalents) is added over a 5 minute period. The mixture is heated to 220°C over 1.5 hours and maintained at temperature for 6.5 hours while distillates are removed. The mixture is allowed to cool to 150°C and filtered using 120 g filter aid to provide 6.56 g of intermediate material.

[0029] The intermediate material, 830 g, 1.18 equivalents, in 400 g toluene, is charged to a 3 L flask, equipped as above, including a caustic trap for H_2S removal. The mixture is heated to 40°C over 30 minutes, then MoO_3 (68.2 g, 0.47 equivalents) and water (30 g) are added with stirring. The reaction mixture is heated to 65°C. Heating is discontinued and carbon disulfide (99.2 g, 1.3 equivalents) is added dropwise to the mixture over 15 minutes. The mixture is then stirred and slowly heated to 85°C and maintained at this temperature for 24 hours. The reaction mixture is vacuum stripped to 145°C / 1.3 kPa (10 mm Hg) over 1 hour. The residue is allowed to cool to 100°C. To the residue is added 111.3 g of a C_{16}—C_{19} alpha olefin while stirring. The reaction mixture is heated to 125°C and stirred for 6 hours, then vacuum stripped to 125°C / 53 kPa (400 mm Hg) over 1 hour. The residue, filtered through a filter aid, is the product.

Example B

[0030] Example A is substantially repeated except that the polyethyleneamine bottoms are replaced by an equivalent amount of tetraethylene pentamine.

[0031] The amount of the molybdenum salt in the final lubricant composition is an amount suitable to provide 50 to 4000 or 50 to 3000 or 50 to 2000 parts per million by weight Mo to the composition. Other amounts will provide 100 to 1500 parts, 125 to 1300 parts, 140 to 500 parts, or 150 to 350 parts per million by weight. The amount of the molybdenum compound to provide these levels of Mo will, of course, depend on the specific identity of the compound. Typically the amount of the salt can be 0.025 to 1 parts by weight per 100 parts of the base oil, or more specifically 0.05 to 0.75 parts, 0.062 to 0.65 parts, 0.07 to 0.25 parts, or 0.75 to 0.38 parts. Its amount in a concentrate will be increased, for instance, to 0.5 to 10 parts.

[0032] Another component of the present invention is a monoester (or partial ester) of a polyol and an aliphatic carboxylic acid, typically an acid containing 12 to 24 carbon atoms.

[0033] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol; preferably, diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol and dipentaerythritol.

[0034] The aliphatic carboxylic acids which form the esters are those acids containing 12 to 24 carbon atoms. Such acid can be characterized by the following general formula: R_1-COOH

wherein R_1 is a hydrocarbyl group, which can be a straight chain hydrocarbyl group, a branched chain or cyclic-containing hydrocarbyl group, or mixtures thereof. Straight chain hydrocarbyl group containing 12 to 24 carbon atoms are preferred, for instance, 14 to 20 or 16 to 18 carbon atoms. Such acids can be used in combination with acids with more or fewer carbon atoms as well.

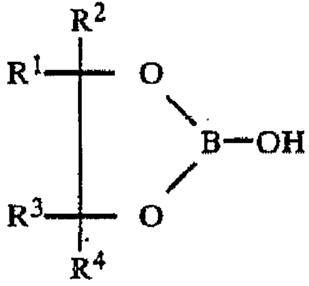
[0035] Generally the acid R_1-COOH is a monocarboxylic acid since polycarboxylic acids tend to form polymeric products if the reaction conditions and amounts of reactants are not carefully regulated. Mixtures of monocarboxylic acids and minor amounts of dicarboxylic acids or anhydrides, however, can be used in preparing the esters. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0036] The carboxylic esters are prepared by the very well-known reaction of at least one carboxylic acid (or reactive equivalent thereof, such as ester, halide, or anhydride) with at least one of the above-described polyhydroxy compounds.

[0037] The esters used in the present invention are in particular the monoesters of such polyols and such carboxylic acids. A preferred ester is glycerol monooleate. It is to be understood that glycerol monooleate, as is the case with other such materials, in its commercially available grade, is a mixture which includes such materials as glycerol, oleic acid, other long chain acids, glycerol dioleate, and glycerol trioleate. The commercial material is believed to include about 60 ± 5 percent by weight of the chemical species "glycerol monooleate," along with 35 ± 5 percent glycerol dioleate, and less than about 5 percent trioleate and oleic acid. The amounts of the monoesters, described below, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture. Similar materials are available under the name UNIFLEX 1803 ™ from Arizona Chemical.

[0038] The amount of the polyol ester in the compositions of the present invention is typically 0.03 to 0.2 parts per 100 parts of the oil of lubricating viscosity. Alternative amounts are 0.05 to 1.0, or 0.7 to 0.75, or 0.1 to 0.3, or about 0.15 parts per 100 parts of the oil. Its amount in a concentrate will be correspondingly increase, for instance, to 0.3 to 10 parts

[0039] Another component of the present invention is a borated epoxide containing 12-24 carbon atoms. This material can alternatively described as a borate ester of a vicinal diol containing 12 to 24 carbon atoms. Such a material may be represented by the structures



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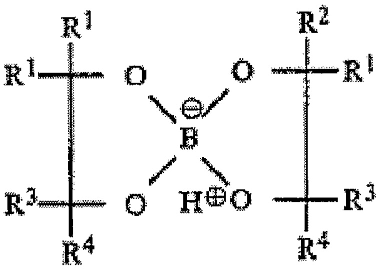


wherein each of R^1, R^2, R^3, and R^4 are independently hydrogen or an aliphatic radical, or any two thereof together with the carbon atom or atoms to which they are attached form a cyclic radical. Preferably at least one of the R groups is an alkyl group containing at least 8 or at least 10 carbon atoms. In one embodiment one of the R groups is such an alkyl group and the remaining R groups are hydrogen. Borated epoxides are described in detail in U.S. Pat. No. 4,584,115. Borated epoxides are generally prepared by reacting an epoxide with a boron source such as boric acid or boron trioxide. Borated epoxides are not themselves epoxides, but are the ring-opened boron-containing reaction products of epoxides. Suitable epoxides include commercial mixtures of C_{14-16} or C_{14-18} or C_{16-18} epoxides, which can be purchased from Elf-Atochem or Union Carbide and which can be prepared from the corresponding olefins by known methods. Purified epoxy compounds such as 1,2-epoxyhexadecane can be purchased from Aldrich Chemicals. The borated compounds are prepared by blending the boron compound and the epoxide and heating them at a suitable temperature, typically 80° to 250°C, until the desired reaction has occurred. An inert liquid, such as toluene, xylene, or dimethylformamide can be used as a reaction medium. Water is formed and is typically distilled off during the reaction. Alkaline reagents can be used to catalyze the reaction. A preferred borated epoxide is the borated epoxide of a predominantly 16 carbon olefin.

[0040] The amount of the borate ester is typically an amount which will provide 30 to 2000 parts per million by weight boron to the composition, alternatively 40 to 1500 ppm, 50 to 1200 ppm, or 60 to 800 ppm. Alternatively expressed, the amount can be 0.05 to 2.0 parts by weight of the composition, alternatively 0.1 to 1.75 percent, 0.2 to 1.5 percent, 0.1 to 1.2 percent, or about 1 percent. Its amount in a concentrate will be correspondingly increased to, for instance, 0.5 to 20 parts.

[0041] Additional materials which may individually also be present (or which may be absent) include those typically found in lubricant formulations, such as dispersants, overbased detergents, metal salts of dialkyldithiophosphates, sulfurized oils, and other boron compounds (other than a borate ester of a vicinal diol containing 12 to 24 carbon atoms described above).

[0042] Dispersants are well known in the field of lubricants and include primarily what are sometimes referred to as "ashless" dispersants because (prior to mixing in a lubricating composition) they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant. Dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain.

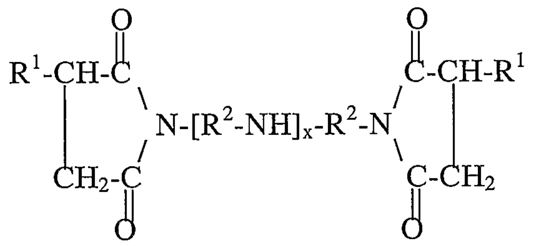
[0043] One class of dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde.

[0044] Another class of dispersant is high molecular weight esters. These materials are similar to the above-described Mannich dispersants or the succinimides described below, 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.

[0045] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0046] A preferred class of dispersants is the carboxylic dispersants. Carboxylic dispersants include succinic-based dispersants, which are the reaction product of a hydrocarbyl substituted succinic acylating agent with an organic hydroxy compound or, preferably, an amine containing at least one hydrogen attached to a nitrogen atom, or a mixture of said hydroxy compound and amine. The term "succinic acylating agent" refers to a hydrocarbon-substituted succinic acid or succinic acid-producing compound (which term also encompasses the acid itself). Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

[0047] Succinic based dispersants, typically known as succinimide dispersants, have a wide variety of chemical structures including typically structures such as



In the above structure, each R1 is independently a hydrocarbyl group, preferably a polyolefin-derived group having an $\overline{M}_n$ of 500 or 700 to 10,000. Typically the hydrocarbyl group is an alkyl group, frequently a polyisobutyl group with a molecular weight of 500 or 700 to 5000, preferably 1500 or 2000 to 5000. The R^2 are alkenyl groups, commonly ethylenyl (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.

[0048] The amines which are reacted with the succinic acylating agents to form the carboxylic dispersant composition can be monoamines or polyamines and will normally be characterized by the presence within their structure of at least one H-N< group, that is at least one primary (i.e., H_2N-) or secondary amino (i.e., H-N<) group. Examples of monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleyl-amine, N-methyloctylamine, dodecylamine, and octadecylamine. Examples of polyamines include alkylene polyamines such as ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(-trimethylene) triamine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful. Tetraethylene pentamine is particularly useful. Hydroxyalkyl-substituted alkylene amines, i.e., alkylene amines having one or more hydroxyalkyl substituents on the nitrogen atoms, likewise are useful.

[0049] Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892.

[0050] The dispersants may be borated materials. Borated dispersants are well-known materials and can be prepared by treatment with a borating agent such as boric acid. Typical conditions include heating the dispersant with boric acid at 100 to 150°C. The dispersants may also be treated by reaction with maleic anhydride.

[0051] The amount of the dispersant in a completely formulated lubricant, if present, will typically be 0.5 to 10 percent by weight, preferably 1 to 8 percent by weight, and more preferably 3 to 7 percent by weight. Its concentration in a concentrate will be correspondingly increased, to, e.g., 5 to 80 weight percent.

[0052] Detergents are generally salts of organic acids, which are often overbased. Metal overbased salts of organic acids are widely known to those of skill in the art and generally include metal salts wherein the amount of metal present exceeds the stoichiometric amount. Such salts are said to have conversion levels in excess of 100% (i.e., they comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal" or "neutral" salt). They are commonly referred to as overbased, hyperbased or superbased salts and are usually salts of organic sulfur acids, organic phosphorus acids, carboxylic acids, phenols or mixtures of two or more of any of these. As a skilled worker would realize, mixtures of such overbased salts can also be used.

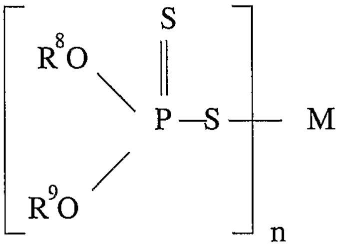
[0053] The terminology "metal ratio" designates the ratio of the total chemical equivalents of the metal in the overbased salt to the chemical equivalents of the metal in the salt which would be expected to result in the reaction between the organic acid to be overbased and the basic reacting metal compound according to the known chemical reactivity and stoichiometry of the two reactants. Thus, in a normal or neutral salt the metal ratio is one and, in an overbased salt, the metal ratio is greater than one. The overbased salts used as component (A) in this invention usually have metal ratios of at least 3:1. Typically, they have ratios of at least 12:1. Usually they have metal ratios not exceeding 40:1. Typically, salts having ratios of 12:1 to 20:1 are used.

[0054] Overbased compositions are well known and can be prepared based on a variety of well known organic acidic materials including sulfonic acids, carboxylic acids (including substituted salicylic acids), phenols, phosphonic acids, and mixtures of any two or more of these. These materials and methods for overbasing of them are well known from numerous U.S. Patents including 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 and need not be further described in detail.

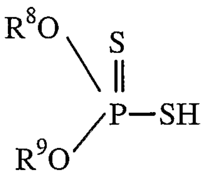
[0055] Preferred overbased materials include overbased phenates derived from the reaction of an alkylated phenol; overbased sulfonates derived from an alkylated aryl sulfonic acids; also overbased carboxylates derived from fatty acids; overbased alkyl-substituted salicylates; overbased saligenin derivatives as described in U.S. patent 6,310,009; and overbased salixarates as described in U.S. Patent 6,200,936 and PCT Publication WO 01/56968.

[0056] The amount of the detergent component in a completely formulated lubricant, if present, will typically be 0.5 to 10 percent by weight, preferably 1 to 7 percent by weight, and more preferably 1.2 to 4 percent by weight. Its concentration in a concentrate will be correspondingly increased, to, e.g., 5 to 65 weight percent.

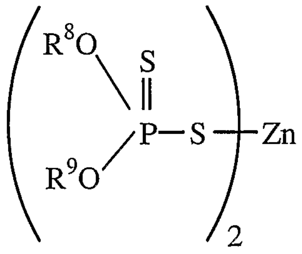
[0057] Metal salts of dialkyldithiophosphates are typically materials of the formula



wherein R8 and R9 are independently hydrocarbyl groups containing 3 to 30 carbon atoms. They are well known materials which are readily obtainable by the reaction of phosphorus pentasulfide and an alcohol or phenol to form an O,O-dihydrocarbyl phosphorodithioic acid corresponding to the formula



[0058] The metal M, having a valence n, is generally aluminum, lead, tin, manganese, cobalt, nickel, zinc, or copper, and most preferably zinc. The basic metal compound is thus preferably zinc oxide, and the resulting metal compound is represented by the formula

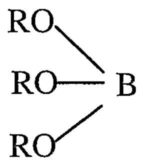


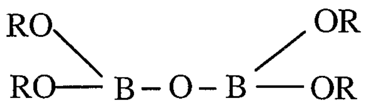
[0059] The R^8 and R^9 groups are independently hydrocarbyl groups that are preferably free from acetylenic and usually also from ethylenic unsaturation. They are typically alkyl, cycloalkyl, aralkyl or alkaryl group and have 3 to 20 carbon atoms, preferably 3 to 16 carbon atoms and most preferably up to 13 carbon atoms, e.g., 3 to 12 carbon atoms. The alcohols which react to provide the R^8 and R^9 groups can be one or more primary alcohols, one or more secondary alcohols, a mixture of secondary alcohol and primary alcohol. A mixture of two secondary alcohols such as isopropanol and 4-methyl-2-pentanol is often desirable.

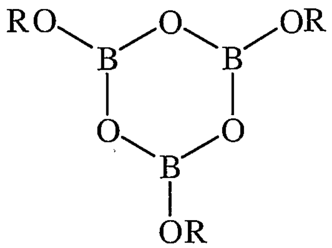
[0060] The amount of the metal dialkyldithiophosphate in a completely formulated lubricant, if present, will typically be 0.1 to 5 percent by weight, preferably 0.3 to 2 percent by weight, and more preferably 0.5 to 1.5 percent by weight. Its concentration in a concentrate will be correspondingly increased, to, e.g., 5 to 60 weight percent.

[0061] Sulfurized oils include sulfurized vegetable oils, sulfurized animal oils such as sulfurized lard oil, and sulfurized olefins such as sulfurized $C_{16\text{-}18}$ olefins, and mixtures of such materials. Sulfurized oils are useful for their antioxidant, antiwear, friction modifying, and extreme pressure protective properties. They can be prepared by well-known methods, such as by treating the appropriate oils, fatty acids, olefins, or mixtures thereof, with sulfur and/or sodium sulfide or hydrosulfide, in the presence of such materials as sodium hydroxide and phosphoric acid.

[0062] The other optional boron compounds include those disclosed in PCT publication WO02/062930, including borate esters of any of the general formulae







where each R is independently hydrogen or, preferably, an organic group, e.g., a hydrocarbyl or an alkyl group, or where any two adjacent R groups may together form a cyclic ring

[0063] An example of such a boron compound is 2-ethylhexyl borate. Others include materials represented by the formulas $B(OC_5H_{11})_3$ or $B(OC_4H_9)_3$. Another example is a phenolic borate available from Crompton Corporation under the trade designation LA-2607.

[0064] Other materials include antifoam agents, antioxidants (e.g., hindered phenols, alkylated diphenylamines), anti-wear agents, extreme pressure agents, pour point depressants, rust inhibitors, corrosion inhibitors, friction modifiers, and antioxidants. (Antioxidants include hindered phenols, ester-containing hindered phenols as disclosed in U.S. Patent 6,559,105, alkylated diphenylamines, and reaction products of a sulfur source and a Diels-Alder adduct, which in turn can be prepared from a dienophile having a carboxylic ester group.) These and other materials used in lubricants are commercially available and many of them are described in greater detail in C. V. Smalheer and R. Kennedy Smith, "Lubricant Additives," Lezius-Hiles Co., Cleveland, Ohio, 1967, especially pages 1-12.

[0065] 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:

[0066] 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);

[0067] 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);

[0068] 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.

[0069] 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 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 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

[0070] Example 1. A racing oil formulation is prepared by mixing the following components:

90 parts (by weight) 4 mm^2/s (4 cSt) synthetic polyalphaolefin oil

10 parts synthetic ester oil (Emery™ 2969B)

– together to form a 0W-10 base oil; and –

0.85 parts molybdenum dithiocarbamate, based on di-2-ethylhexylamine, to impart 350 ppm Mo to the composition (Adeka Sakuralube™ 100, commercial material including any diluent commercially present)

0.25 parts glycerol monooleate (commercial grade as described above)

1.0 part borated C_{16-18} epoxides (neat)

1.0 part ester and imide dispersant(s) (including 45 percent oil)

1.0 part succinimide dispersant(s) (including 53 percent oil)

1.0 part overbased calcium alkylsalicylate detergent, 165 TBN (including 40% oil)

0.6 parts zinc dialkyldithiophosphate (including 9 percent oil)

1.5 parts sulfurized lard oil composition (including a mixture of oils)

[0071] Example 2. Lubricating formulations for highway vehicles are prepared by mixing the following components:

100 parts by weight mineral oil base stock, including viscosity modifier

0.85 parts molybdenum dithiocarbamate, based on di-2-ethylhexylamine, to impart 350 ppm Mo to the composition (as described above)

0.25 parts glycerol monooleate (commercial grade as described above)

1.0 part borated C_{16-18} epoxides (neat)

0.25 to 3.0 parts succinimide dispersant(s) (oil free basis)

0.3 to 1.0 parts zinc dialkyldithiophosphate (oil free basis)

0.4 to 3.8 parts antioxidants

0.7 to 2.0 parts calcium overbased detergent(s) (oil free basis)

0 to 0.4 parts fatty ester friction modifier

0 to 3 parts tri-2-ethylhexyl borate

40-100 ppm silicone foam inhibitor

and incidental diluent oil.

[0072] Example 3. Alternative formulations for highway vehicles are prepared as in Example 2, except using:

0.25 parts by weight of the molybdenum dithiocarbamate

0.075 parts of the glycerol monooleate

0.3 parts of the borated epoxides

[0073] Examples 4 – 7. Three reference lubricants (comparative) and one lubricant of the present invention are prepared, having the composition shown in the table below, and are subjected to various performance tests as reported in the table and further described below. Amounts are reported in parts per 100 parts base oil and are expressed on an active ingredient (oil-free) basis.

Component or Test	4 (comp.) Baseline	5 (comp.)	6 (comp.)	7
Oil, Group II, 100 N	100	100	100	100
Viscosity Modifier	0.44	0.44	0.44	0.44
Pour Point Depressant	0.11	0.11	0.11	0.11
Additional Diluent Oil	0.49	0.49	0.44	0.99
Succinimide dispersant	2.55	2.55	2.55	3.05
Zinc Dialkyldithiophosphate	0.77	077	0.77	0.77
Antioxidants (blend)	2.44	2.44	2.00 [a]	2.44
Sunflower Oil	0	0.20	0.20	0.20
Overbased Ca Detergent	0.85	0.85	0.65 [b]	0.85
Foam Inhibitor	0.01	0.01	0.01	0.01

Glycerol Monooleate	**0**	**0.20**	**0.20**	**0.45**
Mo Dithiocarbamate	**0**	**0**	**0.15**	**0.15**
Borated Epoxide	**0**	**0**	**0**	**0.25**
Borate Ester (additional)	0	0	0.35	0.25
Sequence IVA, % of baseline	100 (fail)	95 [c] (fail)	12.7 (strong pass)	13.4 (strong pass)
Sequence VIB Fuel Economy (% of baseline):				
FEI 1	100	116	126	147
FEI 2	100	200	221	260
Total FE	100	145	155	186
SRV test, new oil	0.140	0.135	0.129	0.092[d]

a. different antioxidant blend
b. contains 0.14 parts Na detergent and 0.51 parts Ca detergent
c. average of three runs
d. average of two runs: 0.973 and 0.112

[0074] The Sequence IVA engine valve train wear tests is a fired engine-dynamometer lubricant test which evaluates the ability of a lubricant to reduce camshaft lobe wear in a 1994 Nissan model DA24E engine. After 100 cycles of two stages (a 50 minute idle speed stage and a 10 minute 1500 r.p.m. stage) the wear at 7 locations on the cam lobes is measured and averaged. The results in the above table, expressed as % wear of the baseline fluid, show that the lubricant of inventive example 7 exhibits a strong pass.

[0075] The Sequence VIB fuel test (ASTM D 6837) measures the effect of engine oil on fuel economy of passenger cars. The test is conducted using a 4.6 L spark-ignited engine on a dynamometer test stand. The test includes measuring the laboratory engine brake specific fuel consumption under 5 speed/ load/ temperature conditions. Test results are expressed as percent change in weighted fuel consumption relative to the baseline calibration. The results show excellent fuel economy for the lubricant of inventive example 7.

[0076] The SRV test is a reciprocating cylinder-on-disk test that measures and reports the friction coefficient of a lubricant between 100°C and 120°C. The lubricant is heated for minutes while applying a 400 N load with a 1 mm reciprocating stroke. The results show a very low coefficient of friction for the lubricant of inventive example 7.

[0077] 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.

3094R-01

What is claimed is:

1. A lubricant composition comprising:

(a) an oil of lubricating viscosity;

(b) a molybdenum salt;

(c) a monoester of (i) a polyol and (ii) an aliphatic carboxylic acid containing about 12 to about 24 carbon atoms; and

(d) a borated epoxide containing 12 to 24 carbon atoms.

2. The composition of claim 1 wherein the oil of lubricating viscosity is a natural or a synthetic oil composition, optionally containing a viscosity index modifier, selected so as to have an SAE multigrade viscosity rating of 0W-10, 0W-20, 0W-30, 5W-20, 5W-30 or an SAE monograde viscosity rating of 20 or 30.

3. The composition of claim 2 wherein the oil of lubricating viscosity is an API Grade II, III, IV, or V oil.

4. The composition of claim 2 wherein the oil of lubricating viscosity comprises a synthetic oil.

5. The composition of claim 4 wherein the synthetic oil is a blend of a polyalphaolefin and a synthetic ester.

6. The composition of claim 1 wherein the molybdenum salt is a molybdenum dihydrocarbyldithiocarbamate.

7. The composition of claim 1 wherein the molybdenum salt is the product of (a) reacting a carboxylic acid or reactive equivalent thereof having about 8 to about 34 carbon atoms with an alkylene polyamine; and (b) reacting the product of (a) with, in any order, (i) a molybdenum compound and (ii) carbon disulfide, to form a molybdenum dithiocarbamate.

8. The composition of claim 1 wherein the amount of the molybdenum salt is an amount suitable to provide about 50 to about 4000 parts per million by weight Mo to the composition.

9. The composition of claim 1 wherein the monoester comprises glycerol monooleate.

10. The composition of claim 1 wherein the amount of the monoester is about 0.03 to about 2.0 parts by weight per 100 parts of the oil of lubricating viscosity.

11. The composition of claim 1 wherein the borated epoxide is a borate esters of a vicinal diol containing 16-18 carbon atoms.

12. The composition of claim 1 wherein the borate ester of (d) is present in an amount to provide about 30 to about 2000 parts per million by weight of boron to the composition.

13. The composition of claim 1 further comprising at least one dispersant, at least one metal salt of a dialkyldithiophosphate, at least one sulfurized oil, and at least one overbased detergent.

14. The composition of claim 1 further comprising an additional boron-containing compound other than that of (d).

15. A composition prepared by admixing the components of claim 1.

16. A method for lubricating an internal combustion engine, comprising supplying thereto the composition of claim 1.

INTERNATIONAL SEARCH REPORT

In[illegible]tional Application No
PCT/US 03/38385

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10M169/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 03/070863 A (LUBRIZOL CORP) 28 August 2003 (2003-08-28) page 5, line 4 -page 6, line 32; examples B-1,, page 19, line 18 -page 20, line 19; claim 1; table 1 ---	1-16
P,X	EP 1 318 189 A (INFINEUM INTERNAT LTD) 11 June 2003 (2003-06-11) paragraphs ‘0046!,‘0051!-‘0058!,‘0063!,‘0068!,‘0073!,‘0076!; claims 8-10 ---	1-16
X	EP 0 987 311 A (LUBRIZOL CORP) 22 March 2000 (2000-03-22) paragraphs ‘0012!,‘0014!,‘0019!,‘0023!,‘0072!,‘0078!,‘0080!,‘0087!,‘0093!; claim 1 ---	1-5,8, 10-16
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 27 April 2004	Date of mailing of the international search report 06/05/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Bertrand, S

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/119895 A1 (BOURGOGNON HENRI ET AL) 29 August 2002 (2002-08-29) paragraphs ‘0064!,‘0169!,‘0174!,‘0177!,‘0178!,‘0180!, ‘0184!,‘0192!; claims 1,2,9,12,13 ---	1-16
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