

LOW DISPERSANT HIGH VI ENGINE OIL FOR IMPROVED FUEL ECONOMY**BACKGROUND**

[0001] Designing automotive lubricants that improve fuel economy while simultaneously maintaining wear, deposit, and/or varnish control has been a longstanding and important challenge for lubricant manufacturers. While fuel economy improvement can be achieved by decreasing the viscosity of the lubricating oil, this approach appears to be nearing the limits of current equipment capabilities. Various friction modifiers (FM) are used to reduce surface friction in the engine and thereby improve fuel economy, but the use of FM is often curtailed by their detrimental effects such as deposit formation and seal degradation. As such, there is a clear need for new methods of improving fuel economy through new lubricating oil formulations.

SUMMARY

[0002] The present disclosure provides a method of improving fuel economy in an internal combustion engine by lubricating engine components with a composition containing low treat rates of borated dispersant, a molybdenum-based friction modifier such as a molybdenum dithiocarbamate (MoDTC), calcium salicylate detergents, and a comb-shaped viscosity index improver. The viscosity index improver maintains appropriate lubricating oil viscosity even at high engine operating temperatures, while the combination of dispersants, friction modifiers, and salicylate detergents work synergistically to provide wear and deposit protection.

[0003] Significant gains in fuel economy can be achieved using the disclosed high viscosity index lubricating composition while maintaining good wear and deposit control. The disclosed lubricating composition is suitable for use in internal combustion engines equipped with a roller-follower valve train.

[0004] The present disclosure is directed to an automobile engine lubricating composition comprising: a) a major amount of an oil of lubricating viscosity; b) a non-borated dispersant; c) a borated dispersant in an amount sufficient to provide less than about 160 ppm of boron to the lubricating composition, wherein the combination of non-borated dispersant and borated dispersant provide at least about 250 ppm of nitrogen to the lubricating composition; d) molybdenum-containing compounds in an amount sufficient to provide at least about 400 ppm of molybdenum to the lubricating composition, wherein the molybdenum-containing compounds comprises molybdenum dithiocarbamate; e) an overbased calcium salicylate detergent; and f) a viscosity index improver (VII); wherein the high temperature high shear viscosity at 100 °C (HTHS100) of the lubricating composition between 3.0 mPa·s to 4.5 mPa·s.

[0005] The present disclosure is further directed to a method of improving fuel economy in an internal combustion engine equipped with a roller-follower type valve train, the method comprising lubricating the internal combustion engine with a lubricating composition comprising: a) a major amount of an oil of lubricating viscosity; b) a non-borated dispersant; c) a borated dispersant in an amount sufficient to provide less than about 160 ppm of boron to the lubricating composition, wherein the combination of

non-borated dispersant and borated dispersant provide at least about 250 ppm of nitrogen to the lubricating composition; d) molybdenum-containing compounds in an amount sufficient to provide at least about 400 ppm of molybdenum to the lubricating composition, wherein the molybdenum-containing compounds comprises molybdenum dithiocarbamate; e) an overbased calcium salicylate detergent; and f) a viscosity index improver (VII).

[0006] The present disclosure is further directed to a use of a lubricating composition to improve the fuel economy of an internal combustion engine, wherein the lubricating composition comprises: a) a major amount of an oil of lubricating viscosity; b) a non-borated dispersant; c) a borated dispersant in an amount sufficient to provide less than about 160 ppm of boron to the lubricating composition, wherein the combination of non-borated dispersant and borated dispersant provide at least about 250 ppm of nitrogen to the lubricating composition; d) molybdenum-containing compounds in an amount sufficient to provide at least about 400 ppm of molybdenum to the lubricating composition, wherein the molybdenum-containing compounds comprises molybdenum dithiocarbamate; e) an overbased calcium salicylate detergent; and f) a viscosity index improver (VII).

DETAILED DESCRIPTION

[0007] While the disclosure is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the disclosure as defined by the appended claims.

[0008] To facilitate the understanding of the subject matter disclosed herein, a number of terms, abbreviations or other shorthand as used herein are defined below. Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a skilled artisan contemporaneous with the submission of this application.

[0009] As used herein, the following terms have the following meanings, unless expressly stated to the contrary. In this specification, the following words and expressions, if and when used, have the meanings given below.

[0010] A "major amount" means in excess of 50 weight % of a composition.

[0011] A "minor amount" means less than 50 weight % of a composition, expressed in respect of the stated additive and in respect of the total mass of all the additives present in the composition, reckoned as active ingredient of the additive or additives.

[0012] "Active ingredients" or "actives" or "oil free" refer to additive material that is not diluent or solvent.

[0013] All percentages reported are weight % on an active ingredient basis (i.e., without regard to carrier or diluent oil) unless otherwise stated.

[0014] The abbreviation "ppm" means parts per million by weight, based on the total weight of the lubricating composition.

[0015] High temperature high shear viscosity at 100 °C (HTHS100) was determined in accordance with ASTM D6616.

[0016] High temperature high shear viscosity at 150 °C (HTHS150) was determined in accordance with ASTM D4683.

[0017] Shear Stability Index (SSI) is measured in accordance with ASTM D6278.

[0018] The term "metal" refers to alkali metals, alkaline earth metals, or mixtures thereof.

[0019] The terms "oil soluble" means that for a given additive, the amount needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed, or suspended in an oil of lubricating viscosity. Usually, this means that at least 0.001 % by weight of the additive can be incorporated in a lubricating composition.

[0020] An "engine" or a "combustion engine" is a heat engine where the combustion of fuel occurs in a combustion chamber. An "internal combustion engine" is a heat engine where the combustion of fuel occurs in a confined space ("combustion chamber"). A "spark ignition engine" is a heat engine where the combustion is ignited by a spark, usually from a spark plug. This is contrast to a "compression-ignition engine," typically a diesel engine, where the heat generated from compression together with injection of fuel is sufficient to initiate combustion without an external spark.

[0021] A "roller-follower type valve train" is a specific type of mechanism for opening and closing the intake and exhaust valves in an internal combustion engine, comprising a roller ring and a finger follower mechanism interposed between the cam and the rocker arm.

[0022] The term "Total Base Number" or "TBN" as used herein refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity. TBN was determined using ASTM D2896 test.

[0023] Boron, calcium, magnesium, molybdenum, phosphorus, sulfur, and zinc contents were determined in accordance with ASTM D5185.

[0024] Nitrogen content was determined in accordance with ASTM D4629.

[0025] All ASTM standards referred to herein are the most current versions as of the filing date of the present application.

[0026] Unless otherwise specified, all percentages are in weight percent.

[0027] The present disclosure provides a lubricating composition comprising: a) an oil of lubricating viscosity; b) a non-borated dispersant; c) a borated dispersant; d) molybdenum-containing compounds; e) an overbased calcium salicylate detergent; and f) a viscosity index improver (VII); wherein the high temperature high shear viscosity at 100 °C (HTHS100) of the lubricating composition is between 3.0 mPa·s to 4.5 mPa·s. The lubricating composition is particularly suitable for internal combustion engines equipped with a direct acting type valve train or a roller-follower type valve train, and particularly suitable for engines equipped with a roller-follower type valve train.

[0028] Also provided herein are methods of improving fuel economy of an internal combustion engine equipped with a roller-follower type valve train. Also provided is a use of a lubricating composition to improve the fuel economy in an internal combustion engine equipped with a roller-follower type valve train.

Oil of Lubricating Viscosity

[0029] The oil of lubricating viscosity (sometimes referred to as “base stock” or “base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating compositions therefrom, and may be selected from natural and synthetic lubricating oils and combinations thereof.

[0030] Natural oils include animal and vegetable oils, liquid petroleum oils and hydrotreated, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0031] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes; polyphenols (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof. Polymerized olefins can also be derived from bio-derived sources such as hydrocarbon terpenes such as myrcene, ocimene and farnesene which can also be co-polymerized with other olefins and further isomerized if desired.

[0032] Another suitable class of synthetic lubricating oils includes the esters of dicarboxylic acids (e.g., malonic acid, alkyl malonic acids, alkenyl malonic acids, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, fumaric acid, azelaic acid, suberic acid, sebacic acid, adipic acid, linoleic acid dimer, phthalic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0033] Esters useful as synthetic oils may also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0034] Also, esters from bio-derived sources are also useful as synthetic oils.

[0035] The base oil may be derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H₂ and CO using a Fischer-Tropsch

catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed; using processes known to those skilled in the art.

[0036] The base oil may be a renewable or bio-derived engine oil. Examples of such engine oils are disclosed in WO2016061050 and US20190338211, which is incorporated herein by reference.

According to some embodiments, the renewable or bio-derived base oil includes a biobased hydrocarbon, such as an isoparaffinic hydrocarbon derived from hydrocarbon terpenes, such as myrcene, ocimene, and farnesene. In some embodiments, the biobased hydrocarbon is produced from fatty acids or fatty esters.

[0037] Unrefined, refined and re-refined oils can be used in the present lubricating composition.

Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art.

[0038] Re-refined oils may also be obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

[0039] Hence, the base oil which may be used to make the present lubricating composition may be selected from any of the base oils in Groups I-V as summarized in Table 1 below:

Table 1

	Base Oil Properties		
Group	Saturates ^(a) , wt. %	Sulfur ^(b) , wt. %	Viscosity Index ^(c)
Group I	<90 and/or	>0.03	80 to <120
Group II	≥90	≤0.03	80 to <120
Group III	≥90	≤0.03	≥120
Group IV	Polyalphaolefins (PAOs)		
Group V	All other base stocks not included in Groups I, II, III, or IV		

^(a) Determined in accordance with ASTM D2007.

^(b) Determined in accordance with ASTM D2622, ASTM D3120, ASTM D4294 or ASTM D4927.

^(c) Determined in accordance with ASTM D2270.

[0040] Base oils suitable for use herein are any of the variety corresponding to API Group II, Group III, Group IV, and Group V oils and combinations thereof. In some embodiments, base oils suitable for use

include Group III to Group V oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[0041] The oil of lubricating viscosity for use in the lubricating compositions of this disclosure, also referred to as a base oil, may be present in a major amount, e.g., an amount of greater than about 50 wt. %. In some embodiments, the base oil may be present in an amount greater than about 70 wt. %. In some embodiments, the base oil may be present in amounts from about 80 wt. % to about 99.5 wt. %. In some embodiments, the base oil may be present in most amounts from about 85 wt. % to about 98 wt. %. The expression “base oil” as used herein shall be understood to mean a base stock or blend of base stocks which is a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both. The base oil for use herein can be any presently known or later-discovered oil of lubricating viscosity used in formulating lubricating compositions.

[0042] The viscosity of the base oil is dependent upon the application. Accordingly, the viscosity of a base oil for use herein may range from about 2 to about 2000 centistokes (cSt) at 100 °Centigrade (C). Generally, individually the base oils used as engine oils will have a kinematic viscosity range at 100 °C. of about 2 cSt to about 30 cSt, about 3 cSt to about 16 cSt, or about 4 cSt to about 12 cSt.

[0043] The lubricating composition may be a multi-grade oil having a viscosity grade of SAE 0W-8, 0W-12, 0W-16, 0W-20, 0W-26, 0W-30, 0W-40, 0W-50, 0W-60, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, 15W-40, and the like.

[0044] The lubricating composition disclosed herein may include a major amount of an oil of lubricating viscosity. In some embodiments, the oil of lubricating viscosity may be a Group II base oil, a Group III base oil, a Group IV base oil, a Group V base oil, or a combination thereof. In some embodiments, the oil of lubricating viscosity may be a Group III base oil.

[0045] In some embodiments, the lubricating composition may have a high temperature high shear viscosity at 100 °C (HTHS100) from 1.0 mPa·s to 6.5 mPa·s, such as from 1.5 mPa·s to 6.0 mPa·s, from 2.0 mPa·s to 5.5 mPa·s, from 2.5 mPa·s to 5.0 mPa·s, from 2.7 mPa·s to 4.7 mPa·s, or from 3.0 mPa·s to 4.5 mPa·s.

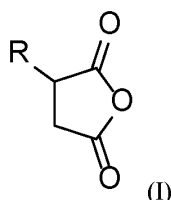
Non-borated Dispersant

[0046] Example lubricating compositions disclosed herein may include a non-borated dispersant. Non-borated dispersants include succinimide dispersants such as those described herein which are not post-treated with a boron source.

[0047] Suitable non-borated dispersants include hydrocarbyl succinimides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acids, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehydes, and polyamines.

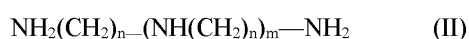
Also suitable are condensation products of polyamines and hydrocarbyl-substituted phenyl acids. Mixtures of these dispersants can also be used.

[0048] In one embodiment, a polyalkenyl bis-succinimide can be obtained by reacting a polyalkenyl-substituted succinic anhydride below:



wherein R is a polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 500 to about 3000, with a polyamine. In one embodiment, R is a polyalkenyl substituent derived from a polyalkene group having a number average molecular weight of from about 1000 to about 2500. In one embodiment, R is a polyisobutenyl substituent derived from a polyisobutene having a number average molecular weight of from about 500 to about 3000. In another embodiment, R is a polyisobutenyl substituent derived from a polyisobutene having a number average molecular weight of from about 1000 to about 2500.

[0049] In some embodiments, amines for reaction to form the succinimide may be polyamines having from 2 to 60 carbon atoms and from 2 to 12 nitrogen atoms per molecule. In some embodiments, the amines include polyalkyleneamines represented by the formula:



wherein n is 2 to 3 and m is 0 to 10. Illustrative examples include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, pentaethylene hexamine and the like, as well as the commercially available mixtures of such polyamines. Amines including other groups such as hydroxy, alkoxy, amide, nitride and imidazoline groups may also be used, as may polyoxyalkylene polyamines. Particularly suitable polyalkylene polyamines are those having the formula: $\text{H}_2\text{N—(R'NH)}_x\text{—H}$ wherein R' is a straight- or branched-chain alkylene group having 2 or 3 carbon atoms and x is 1 to 9. Representative examples of suitable polyalkylene polyamines include ethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentamine, pentaethylene hexamine, and heavy polyamines (e.g., Ethyleneamine E-100, available from Huntsman Company).

[0050] The amines may be reacted with the alkenyl succinic acid or anhydride in conventional ratios of about 1:1 to 10:1 or 1:1 to 3:1 moles of alkenyl succinic acid or anhydride to polyamine, or in a ratio of about 1:1 mole of alkenyl succinic acid or anhydride to polyamine, typically by heating the reactants to from 100 °C to 250 °C, or from 125 °C to 175 °C for 1 to 10 hours. In some embodiments, the amines are reacted by heating the reactants for about 2 to 6 hours.

Borated Dispersant

[0051] Lubricating compositions disclosed herein may include a borated dispersant. The borated dispersant may be present in an amount to provide less than about 300 ppm, about 250 ppm, about 200

ppm, about 180 ppm, or about 160 ppm of boron to the lubricating composition. In some embodiments, the borated dispersant may be present in an amount to provide about 30 ppm to about 300 ppm, about 40 ppm to about 250 ppm, about 50 ppm to about 200 ppm, about 60 ppm to about 190 ppm, about 70 ppm to about 180 ppm, about 80 ppm to about 170 ppm, or about 90 ppm to about 160 ppm of boron to the lubricating composition.

[0052] Some lubricating compositions disclosed herein include a combination of non-borated dispersant and borated dispersant. The combination of non-borated dispersant and borated dispersant may be present in an amount sufficient to provide at least about 100 ppm, about 150 ppm, about 200 ppm, about 210 ppm, about 220 ppm, about 230 ppm, about 240 ppm, or about 250 ppm of nitrogen to the lubricating composition. In some embodiments, the combination of dispersants is present in an amount sufficient to provide about 100 ppm to about 1500 ppm, about 150 ppm to about 1000 ppm, about 200 ppm to about 800 ppm, about 230 ppm to about 700 ppm, about 250 ppm to about 600 ppm, about 270 ppm to about 580 ppm, about 300 to about 560 ppm, or about 320 ppm to about 540 ppm of nitrogen to the lubricating composition.

[0053] The total amount of the non-borated dispersant and borated dispersant present in the lubricating composition may be between about 0.5 wt. % to about 7.0 wt. %, about 0.6 wt. % to about 6.0 wt. %, about 0.7 wt. % to about 5.5 wt. %, about 0.8 wt. % to about 5.0 wt. %, about 0.9 wt. % to about 4.5 wt. %, about 1.0 wt. % to about 4.0 wt. %, about 1.1 wt. % to about 3.8 wt. %, about 1.2 wt. % to about 3.6 wt. %, about 1.4 wt. % to about 3.4 wt. %, or about 1.5 wt. % to about 3.2 wt. %.

[0054] Examples of borated dispersants include borated ashless dispersants such as borated polyalkenyl succinic anhydrides; borated non-nitrogen containing derivatives of a polyalkylene succinic anhydride; borated basic nitrogen compounds selected from the group consisting of succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbyl polyamines, Mannich bases, phosphonoamides, thiophosphonamides and phosphoramides, thiazoles (e.g., 2,5-dimercapto-1,3,4-thiadiazoles, mercaptobenzothiazoles and derivatives thereof), triazoles (e.g., alkyltriazoles and benzotriazoles), copolymers which contain a carboxylate ester with one or more additional polar function, including amine, amide, imine, imide, hydroxyl, carboxyl, and the like (e.g., products prepared by copolymerization of long chain alkyl acrylates or methacrylates with monomers of the above function); and the like and combinations thereof. In some examples, a borated dispersant may be a succinimide derivative of boron such as, for example, a borated polyisobutenyl succinimide.

[0055] Examples of borated ashless dispersants may be borated ashless hydrocarbyl succinimide dispersants prepared by reacting a hydrocarbyl succinic acid or anhydride with an amine as described above. In some examples, the hydrocarbyl succinic acids or anhydrides are those where the hydrocarbyl group is derived from a polymer of a C₃ or C₄ monoolefin, especially a polyisobutylene wherein the polyisobutenyl group has a number average molecular weight (M_n) of from about 700 to about 5,000, or from about 900 to about 2,500. Such dispersants generally have at least 1, or 1 to 2, or 1.1 to 1.8, succinic groups for each polyisobutenyl group. In one embodiment, the oil soluble or oil dispersible borated

polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of from about 550 to about 5000. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of from about 550 to about 4000. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of from about 550 to about 3000. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant is derived from a polyisobutylene group having a number average molecular weight of greater than about 550 to about 2300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of from about 950 to about 2300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of from about 950 to about 1700. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant is derived from a polyisobutylene group having a number average molecular weight of about 2300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant is derived from a polyisobutylene group having a number average molecular weight of about 1700. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of about 1000.

[0056] The boration of alkenyl succinimide dispersants is also well known in the art as disclosed in U.S. Pat. Nos. 3,087,936 and 3,254,025. The succinimide may for example be treated with a boron compound selected from the group consisting of boron, boron oxides, boron halides, boron acids and esters thereof, in an amount to provide from 0.1 atomic proportion of boron to 10 atomic proportions of boron for each atomic proportion of nitrogen in the dispersant.

[0057] The borated product will generally contain from about 0.1 wt. % to about 2.0 wt. %, or from about 0.2 wt. % to about 0.8 wt. % boron based upon the total weight of the borated dispersant. Boron is considered to be present as dehydrated boric acid polymers attaching at the metaborate salt of the imide. The boration reaction is readily carried out adding from about 1 wt. % to about 3 wt. % (based on the weight of dispersant) of said boron compound, such as boric acid, to the dispersant as a slurry in mineral oil and heating with stirring from 135 °C to 165 °C for 1 to 5 hours followed by nitrogen stripping filtration of the product. Alternatively, boric acid may be added to the hot reaction mixture of succinic acid or anhydride and amine while removing water.

Molybdenum-containing Compounds

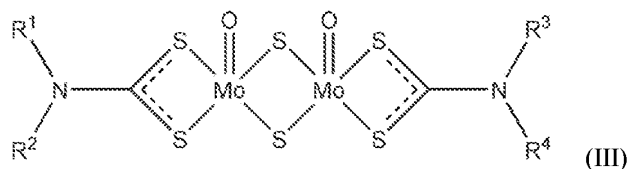
[0058] Lubricating compositions disclosed herein may include molybdenum-containing compounds, wherein the molybdenum -containing compounds include molybdenum dithiocarbamate (MoDTC). The molybdenum-containing compounds additionally may further include a molybdenum-amine complex, a

molybdenum dithiophosphate, or a combination thereof. Suitable molybdenum-containing compounds are described herein.

[0059] The molybdenum-containing compounds may be present in an amount sufficient to provide at least about 200 ppm, about 250 ppm, about 300 ppm, about 350 ppm, about 400 ppm, about 450 ppm, or about 500 ppm of molybdenum to the lubricating composition. In some embodiments the molybdenum-containing compounds may be present in an amount sufficient to provide about 200 ppm to about 2000 ppm, about 300 ppm to about 1800 ppm, about 400 ppm to about 1600 ppm, about 500 ppm to about 1500 ppm, about 600 ppm to about 1400 ppm, about 700 ppm to about 1300 ppm, about 800 ppm to about 1200 ppm, or about 900 ppm to about 1100 ppm of molybdenum to the lubricating composition.

[0060] Molybdenum-containing compounds may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. Molybdenum-containing compounds may include molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiophosphinates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear organo-molybdenum compound, molybdenum esters, molybdenum amides, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be in the form of a stable dispersion. In one embodiment the molybdenum-containing compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the molybdenum-containing compound may be a molybdenum dithiocarbamate.

[0061] Molybdenum dithiocarbamate (MoDTC) is an organomolybdenum compound represented by the following structure:

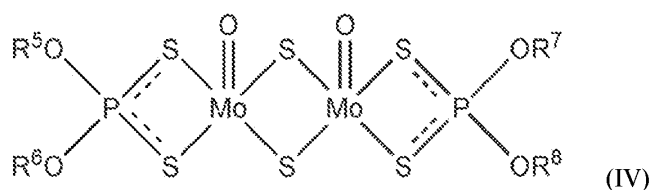


wherein R^1 , R^2 , R^3 , and R^4 are each independently alkyl groups, alkenyl groups, cycloalkyl groups, or cycloalkenyl groups having from 4 to 18 carbon atoms (e.g., 8 to 13 carbon atoms), or aryl groups having from 6 to 18 carbon atoms. The alkyl or alkenyl groups may be straight-chain or branched, and mixtures thereof.

[0062] Generally, MoDTC can be prepared by reacting molybdenum trioxide or a molybdate with an alkali sulfide or an alkali hydrosulfide, and subsequently adding carbon disulfide and a secondary amine to the reaction mixture and reacting the resultant mixture at an adequate temperature. To prepare the asymmetric molybdenum dithiocarbamates, the use of a secondary amine having different hydrocarbon groups or the use of two or more different secondary amines in the above process is sufficient. The symmetric molybdenum dithiocarbamates can also be prepared in a similar manner, but with the use of only one secondary amine.

[0063] Examples of suitable molybdenum dithiocarbamate compounds include, but are not limited to, molybdenum dibutyldithiocarbamate, molybdenum dipentylthiocarbamate, molybdenum dihexyldithiocarbamate, molybdenum dioctyldithiocarbamate, molybdenum didecyldithiocarbamate, molybdenum didodecyldithiocarbamate, molybdenum ditridecyldithiocarbamate, molybdenum di(butylphenyl)dithiocarbamate, and molybdenum di(nonylphenyl)dithiocarbamate.

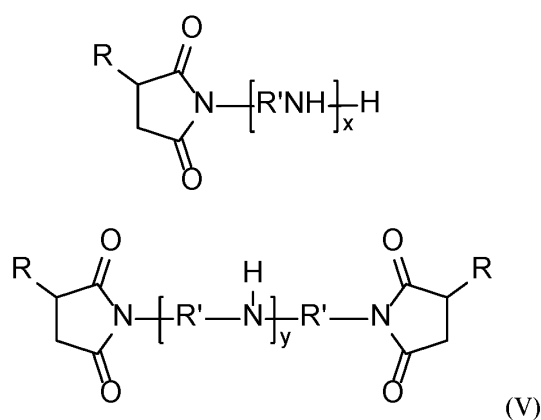
[0064] In some embodiments the molybdenum-containing compounds further include a molybdenum dithiophosphate. Molybdenum dithiophosphate (MoDTP) is an organomolybdenum compound represented by the following structure:



wherein R^5 , R^6 , R^7 , and R^8 are each independently alkyl groups, alkenyl groups, cycloalkyl groups, or cycloalkenyl groups having from 4 to 18 carbon atoms (e.g., 8 to 13 carbon atoms), or aryl groups having from 6 to 18 carbon atoms. The alkyl or alkenyl groups may be straight-chain or branched, and mixtures thereof.

[0065] Examples of suitable molybdenum dithiophosphate compounds include, but are not limited to, molybdenum dibutyldithiophosphate, molybdenum dipentylthiophosphate, molybdenum dihexyldithiophosphate, molybdenum dioctyldithiophosphate, molybdenum didecyldithiophosphate, molybdenum didodecyldithiophosphate, molybdenum ditridecyldithiophosphate, molybdenum di(butylphenyl)dithiophosphate, or molybdenum di(nonylphenyl)dithiophosphate.

[0066] In some embodiments, the molybdenum-containing compounds further include a molybdenum-amine complex. In some embodiments, the molybdenum-amine complex may be a molybdenum succinimide complex. Suitable molybdenum-succinimide complexes are described, for example, in U.S. Patent No. 8,076,275. These complexes are prepared by a process comprising reacting an acidic molybdenum compound with an alkyl or alkenyl succinimide of a polyamine of structures below or mixtures thereof:



Wherein R is a C₂₄ to C₃₅₀ (e.g., C₇₀ to C₁₂₈) alkyl or alkenyl group; R' is an alkylene group having 2 to 3 carbon atoms; x is 1 to 11; and y is 1 to 10. The alkyl or alkenyl groups may be straight-chain or branched, and mixtures thereof.

[0067] Generally, the acidic molybdenum compounds used to prepare the molybdenum succinimide complex are hexavalent. By "acidic" it is meant that the compound will react with a basic nitrogen compound as measured by ASTM D664 or D2896. Representative examples of suitable acidic molybdenum compounds include molybdenum trioxide, molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, (e.g., hydrogen sodium molybdate), MoOCl₄, MoO₂Br₂, Mo₂O₃Cl₆, and the like.

[0068] The succinimides that can be used to prepare the molybdenum succinimide complex are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 3,172,892; 3,219,666; and 3,272,746. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkyl or alkenyl substituted succinic acid or anhydride with a nitrogen containing compound. Some succinimides are those prepared by reacting a polyisobutenyl succinic anhydride of about 70 to about 128 carbon atoms with a polyalkylene polyamine selected from triethylenetetramine, tetraethylenepentamine, and mixtures thereof.

[0069] The molybdenum-succinimide complex may be post-treated with a sulfur source at a suitable pressure and a temperature not to exceed 120 °C to provide a sulfurized molybdenum-succinimide complex. The sulfurization step may be carried out for a period of from about 0.5 to about 5 hours (e.g., 0.5 to 2 hours). Suitable sources of sulfur include elemental sulfur, hydrogen sulfide, phosphorus pentasulfide, organic polysulfides of formula R₂S_x where R is hydrocarbyl (e.g., C₁ to C₁₀ alkyl) and x is at least 3, C₁ to C₁₀ mercaptans, inorganic sulfides and polysulfides, thioacetamide, and thiourea.

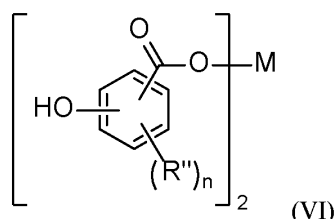
[0070] Suitable examples of molybdenum-containing compounds which may be used include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A, Molyvan™ 2000, and Molyvan™ 855 from R.T. Vanderbilt Co. Ltd., and Sakura-Lube™ S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Additional suitable molybdenum compounds are described in U.S. Pat. No. 5,650,381; US RE37,363 E1; US RE38,929 E1; and US RE40,595 E1, incorporated herein by reference in their entireties.

Calcium Salicylate Detergent

[0071] The lubricating composition of the present disclosure includes an overbased calcium salicylate detergent. The overbased calcium salicylate may be present in an amount sufficient to provide about 300 ppm to about 2500 ppm, about 400 ppm to about 2400 ppm, about 500 ppm to about 2300 ppm, about 600 ppm to about 2200 ppm, about 700 ppm to about 2100 ppm, about 800 ppm to about 2000 ppm,

about 900 ppm to about 1900 ppm, about 1000 ppm to about 1800 ppm, about 1100 ppm to about 1700 ppm, or about 1200 ppm to about 1600 ppm of calcium to the lubricating composition.

[0072] Salicylate detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing water from the reaction product. Detergents made from salicylic acid are one class of detergents prepared from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the following structure:



wherein R'' is a C₁ to C₃₀ (e.g., C₁₃ to C₃₀) alkyl group; n is an integer from 1 to 4; and M is an alkaline earth metal (e.g., Ca or Mg).

[0073] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[0074] Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN) of from 0 to about 80 mg KOH/g. Useful detergents can be neutral, mildly overbased, or highly overbased.

[0075] The terminology "overbased" relates to metal salts, such as metal salts of sulfonates, salicylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may contain more than 100% of the theoretical amount of metal needed to convert the acid to its "normal," "neutral" salt). The expression "metal ratio," often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, salicylic acids, or phenols.

[0076] An overbased detergent has a TBN of about 150 mg KOH/gram or greater, a TBN of about 250 mg KOH/gram or greater, a TBN of about 300 mg KOH/gram or greater, a TBN of about 350 mg KOH/gram or greater, a TBN of about 375 mg KOH/gram or greater, or a TBN of about 400 mg KOH/gram or greater based on the detergent concentrate.

[0077] The overbased detergent may have a metal to substrate ratio of from 1.1:1, from 2:1, from 4:1, from 5:1, from 7:1, or from 10:1.

Magnesium Detergent

[0078] The lubricating composition of the present disclosure may further include a magnesium detergent. The magnesium detergent of the present disclosure may be present in an amount sufficient to provide about 100 ppm to about 2200 ppm, about 200 ppm to about 1000 ppm, about 250 ppm to about 900 ppm, about 300 ppm to about 800 ppm, about 350 ppm to about 700 ppm, about 400 ppm to about 600 ppm, or about 450 ppm to about 550 ppm of magnesium to the lubricating composition.

[0079] In some embodiments, the magnesium detergents include magnesium sulfonates, magnesium phenates, and magnesium salicylates, especially magnesium sulfonates and salicylates. In some embodiments, the magnesium detergent is a magnesium sulfonate. The magnesium sulfonate may be neutral, mildly overbased, or highly overbased.

[0080] 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. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to 80 or more carbon atoms (e.g., about 16 to 60 carbon atoms) per alkyl substituted aromatic moiety.

[0081] Phenates can be prepared by reacting an alkaline earth metal hydroxide or oxide (e.g., CaO, Ca(OH)₂, MgO, or Mg(OH)₂) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight or branched chain C₁ to C₃₀ (e.g., C₄ to C₂₀) alkyl groups, or mixtures thereof. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched chain. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (e.g., elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0082] Salicylates may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing water from the reaction product. Detergents made from salicylic acid are one class of detergents prepared from carboxylic acids. Useful salicylates include long chain alkyl salicylates.

Viscosity Index Improver (VII)

[0083] The lubricating composition of the present disclosure includes a viscosity index improver (VII). In some embodiments, the viscosity index improver is a linear (conventional) polymethacrylate (PMA) or a comb-shaped polymethacrylate (PMA).

[0084] The viscosity index improver of the lubricating composition has a shear stability index (SSI) of less than or equal to 50.0, less than or equal to 40.0, less than or equal to 30.0, less than or equal to 25.0, less than or equal to 20.0, less than or equal to 15.0, less than or equal to 10.0, less than or equal to 5.0, or less than or equal to 1.0 as measured by ASTM method D6278. In some embodiments, the SSI of the

viscosity index improver is between 0.1 to 1.0, between 0.2 to 0.9, between 0.3 to 0.8, or between 0.4 to 0.7. In some embodiments, the SSI of the viscosity index improver is between 1.0 to 50.0, between 5.0 to 40.0, or between 10.0 to 35.0, or between 20.0 to 30.0.

[0085] The amount of viscosity index improver present in the lubricating composition may be between about 2.0 wt. % to about 15.0 wt. %, about 4.0 wt. % to about 12.5 wt. %, about 5.0 wt. % to about 11.0 wt. %, about 5.5 wt. % to about 10.5 wt. %, about 6.0 wt. % to about 10.0 wt. %, about 6.5 wt. % to about 9.5 wt. %, about 6.8 wt. % to about 9.0 wt. %, or about 7.0 wt. % to about 8.5 wt. %.

[0086] Linear, or conventional polymethacrylates (PMA) are generally synthesized by simple free-radical copolymerization of a mixture of different alkyl methacrylates. In order to impart oil solubility, linear PMA viscosity index improvers typically contain methacrylate repeat units with alkyl side chains having hydrocarbon groups, e.g. an alkyl chain comprising 6-24 carbon atoms.

[0087] Non-limiting examples of linear PMAs include Viscoplex® Viscosity Index Improver 12-075, 12-115, and/or 12-199, which are available from Evonik RohMax USA, Inc.

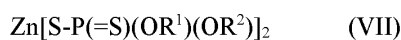
[0088] A comb-shaped polymer includes relatively long side chains being bonded to a polymeric main chain, frequently also known as the backbone. Comb-shaped PMAs are methacrylate-based polymers which have at least one repeat methacrylate unit derived from polyolefin-based macromonomers, which typically have a number average molecular weight (M_n) of greater than about 500 g/mol. The exact proportion is evident via the molar degree of branching. The macromonomers contain olefinic repeat units which are derived from alkenes or alkadienes, for example ethylene, propylene, n-butene, isobutene, butadiene, isoprene.

[0089] Comb-shaped PMAs are described as set forth in US 2017/0298287A1 and JP 2019014802, the disclosures of which is incorporated herein by reference. Non-limiting examples of comb-shaped PMAs include Viscoplex® Viscosity Index Improver 3-201 and/or 3-162, which are available from Evonik RohMax USA, Inc.

[0090] Viscoplex® 3-201 is a comb-shaped PMA that has a weight average molecular weight (M_w) of 420,000 g/mol, a number average molecular weight (M_n) of 70,946 g/mol, and a M_w/M_n of 5.92. The compound has at least a constituent unit derived from a macromonomer having a M_n of 500 or more. Comb-shaped PMA is present in an amount of 19 wt. %, based on the total weight of the compound. Viscoplex® 3-162 is a comb-shaped PMA that has a weight average molecular weight (M_w) of 399,292 g/mol, a number average molecular weight (M_n) of 205,952 g/mol, a M_w/M_n of 1.94, and a SSI of <1.0 as measured by ASTM method D6278.

Zinc Dithiophosphate (ZnDTP)

[0091] The lubricating composition of the present disclosure may further include a zinc dithiophosphate (ZnDTP). Zinc dithiophosphates are antiwear agents that reduce wear of engine parts, having the following formula:



wherein R^1 and R^2 may be the same or different hydrocarbyl radicals having from 1 to 18 (e.g., 2 to 12) carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. In some embodiments, the R^1 and R^2 groups are alkyl groups having from 2 to 8 carbon atoms (e.g., the alkyl radicals may be ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl, or 2-ethylhexyl). In order to obtain oil solubility, the total number of carbon atoms (i.e., R^1+R^2) will be at least 5. The zinc dihydrocarbyl dithiophosphate can therefore include zinc dialkyl dithiophosphates (ZDDP). The zinc dialkyl dithiophosphate can be a primary ZnDTP containing primary alkyl groups, or secondary zinc dialkyl dithiophosphate containing secondary alkyl groups, or mixtures thereof. In some embodiments, the zinc dithiophosphate is a secondary zinc dithiophosphate.

[0092] In some embodiments, the zinc dithiophosphate may be present in an amount sufficient to provide about 200 ppm to about 1500 ppm, about 300 ppm to about 1400 ppm, about 400 ppm to about 1300 ppm, about 500 ppm to about 1200 ppm, about 600 ppm to about 1100 ppm, about 700 ppm to about 1000 ppm, about 750 ppm to about 950 ppm, or about 800 to about 900 ppm of zinc to the lubricating composition.

Other Additives

[0093] The lubricating compositions of the present disclosure may also contain other conventional additives that can impart or improve any desirable property of the lubricating composition in which these additives are dispersed or dissolved. Any additive known to a person of ordinary skill in the art may be used in the lubricating compositions disclosed herein. Some suitable additives have been described in Mortier et al., "Chemistry and Technology of Lubricants", 2nd Edition, London, Springer, (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications", New York, Marcel Dekker (2003), both of which are incorporated herein by reference. For example, the lubricating compositions can be blended with antioxidants, anti-wear agents, detergents such as metal detergents, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, corrosion-inhibitors, dispersants, multifunctional agents, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating compositions of the disclosure by the usual blending procedures.

[0094] In the preparation of lubricating formulations, it is common practice to introduce the additives in the form of about 10 wt. % to about 100 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent.

[0095] Usually these concentrates may be diluted with about 3 to about 100, e.g., 5 to 40, parts by weight of lubricating oil per part by weight of the additive package in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend.

[0096] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is a friction modifier, a functionally effective amount of this friction modifier would be an amount sufficient to impart the desired friction modifying characteristics to the lubricant.

[0097] In general, the concentration of each of the additives in the lubricating composition, when used, may range from about 0.001 wt. % to about 20 wt. %, from about 0.01 wt. % to about 15 wt. %, from about 0.1 wt. % to about 10 wt. %, from about 0.005 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 2.5 wt.%, based on the total weight of the lubricating composition. Further, the total amount of the additives in the lubricating composition may range from about 0.001 wt.% to about 20 wt.%, from about 0.01 wt.% to about 10 wt.%, or from about 0.1 wt.% to about 5 wt.%, based on the total weight of the lubricating composition.

EXAMPLES

[0098] The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present disclosure.

Example 1

[0099] A lubricating composition was prepared by blending the following components:

- a) 1.50 wt. % of a borated dispersant
- b) 0.25 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 7.90% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0100] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.25 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.23 mPa·s.

Example 2

[0101] A lubricating composition was prepared by blending the following components:

- a) 2.50 wt. % of a borated dispersant
- b) 0.50 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP

- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 7.50% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0102] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.42 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.32 mPa·s.

Example 3

[0103] A lubricating composition was prepared by blending the following components:

- a) 1.50 wt. % of a borated dispersant
- b) 1.50 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 7.50% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0104] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.42 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.32 mPa·s.

Example 4

[0105] A lubricating composition was prepared by blending the following components:

- a) 1.50 wt. % of a borated dispersant
- b) 0.25 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 7.30% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0106] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.49 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.36 mPa·s.

Comparative Example 1

[0107] A lubricating composition was prepared by blending the following components:

- a) 0.75 wt. % of a borated dispersant
- b) 0.13 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 9.40% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0108] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.32 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.34 mPa·s.

Comparative Example 2

[0109] A lubricating composition was prepared by blending the following components:

- a) 0.38 wt. % of a borated dispersant
- b) 0.063 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 9.65% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0110] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.28 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.32 mPa·s.

Comparative Example 3

[0111] A lubricating composition was prepared by blending the following components:

- a) 3.00 wt. % of a borated dispersant
- b) 0.50 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 7.80% of a comb-shaped viscosity index improver

- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0112] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.50 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.31 mPa·s.

Comparative Example 4

[0113] A lubricating composition was prepared by blending the following components:

- a) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- b) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- c) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- d) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- e) 10.50% of a comb-shaped viscosity index improver
- f) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0114] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.30 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.37 mPa·s.

Comparative Example 5

[0115] A lubricating composition was prepared by blending the following components:

- a) 0.25 wt. % of a borated dispersant
- b) 1.50 wt. % of a non-borated dispersant
- c) approximately 1410 ppm, in terms of Ca content, of a Ca salicylate detergent
- d) approximately 470 ppm, in terms of Mg content, of a Mg sulfonate detergent
- e) approximately 850 ppm, in terms of Zn content, of a secondary ZnDTP
- f) approximately 1000 ppm, in terms of Mo content, of molybdenum compounds
- g) 7.30% of a comb-shaped viscosity index improver
- h) mixture of base oil A (Yubase 4 Plus) and base oil B (Yubase 3)

[0116] The remainder of the lubricating composition includes a minor amount of antioxidant and foam inhibitor. The finished oil had a high temperature high shear viscosity at 100 °C (HTHS100) of 4.50 mPa·s and a high temperature high shear viscosity at 150 °C (HTHS150) of 2.36 mPa·s.

JASO M366 Fuel Economy Test

[0117] The lubricating compositions above were tested for their fuel economy performance in a gasoline motored engine with roller follower valvetrain (Toyota 2ZR-FXE).

[0118] The detailed configuration of equipment, baseline calibration (BC) oil description, and conditions of the Toyota 2ZR-FXE test can be found in JASO M366 test method. The test oils are pre-conditioned

in the engine operating at 1350 rpm for 10 hours at an oil temperature of 88 °C. The fuel economy measurement consist of six steady-state operational conditions that represent the WLTC (phase low, medium, and high). The fuel consumption (kg/h) is calculated as a total value of stage fuel consumptions with weighting factors.

[0119] The fuel economy improvement (FEI) is calculated for the candidate oil test as relative improvement (% change) to the average of two BC oils as shown below. A higher FEI value indicates overall better fuel economy performance.

$$[FEI(\%)] = \frac{([TFCBCB(\text{kg/h})] + [TFCBCA(\text{kg/h})]) \div 2 - [TFCCAN(\text{kg/h})]}{([TFCBCB(\text{kg/h})] + [TFCBCA(\text{kg/h})]) \div 2} \times 100$$

FEI : Fuel Economy Improvement (%)

TFCCAN : Total Fuel Consumption of Candidate Oil (kg/h)

TFCBCB : Total Fuel Consumption of BC Before (kg/h)

TFCBCA : Total Fuel Consumption of BC After (kg/h)

[0120] The results of the fuel economy tests are shown below in Table 2. The Fuel Economy Improvement (FEI) results show that upon increasing the amount of boron from the borated dispersant above about 160 ppm, as seen in comparative example 3, the FEI no longer falls within the acceptable limit of >1.01%. The nitrogen content as provided by the combination of non-borated dispersant and borated dispersant must be above about 320 ppm to maintain FEI within acceptable limits, as exhibited by comparative examples 1, 2, 4, and 5.

Table 2

	Units	Ex 1	Ex 2	Ex 3	Ex 4	Comp Ex 1	Comp Ex 2	Comp Ex 3	Comp Ex 4	Comp Ex 5
Borated Dispersant	wt. %	1.50	2.50	1.50	1.50	0.75	0.38	3.00	0.00	0.25
Non- Borated Dispersant	wt. %	0.25	0.50	1.50	0.25	0.13	0.063	0.50	0.00	1.50
B (from borated dispersant)	ppm	90	160	90	90	50	20	190	0	20
N (from dispersants)	ppm	320	540	440	320	160	80	640	0	200
Ca	ppm	1410	1410	1410	1410	1410	1410	1410	1410	1410

Mg	ppm	470	470	470	470	470	470	470	470	470
Zinc	ppm	850	850	850	850	850	850	850	850	850
Mo (from MoDTC)	ppm	800	800	800	800	800	800	800	800	800
Mo (total)	ppm	1000	1000	1000	1000	1000	1000	1000	1000	1000
VII	wt. %	7.90	7.50	7.50	7.30	9.40	9.65	7.80	10.50	7.30
Base oil A	wt. ratio	62	62	62	100	62	62	62	62	100
Base oil B	wt. ratio	38	38	38	0	38	38	38	38	0
HTHS150	mPas	2.23	2.32	2.32	2.36	2.34	2.32	2.31	2.37	2.36
HTHS100	mPa·s	4.25	4.42	4.42	4.49	4.32	4.28	4.50	4.30	4.50
FEI	%	1.83	1.61	1.29	1.14	0.88	0.90	1.01	0.91	0.86

[0121] While the disclosure is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the disclosure as defined by the appended claims.

[0122] Note that not all of the activities described in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed is not necessarily the order in which they are performed.

[0123] Benefits, other advantages, and solutions to problems have been described herein with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all the claims.

[0124] The specification and illustrations of the embodiments described herein are intended to provide a general understanding of the structure of the various embodiments.

[0125] The specification and illustrations are not intended to serve as an exhaustive and comprehensive description of all the elements and features of formulations, compositions, apparatus and systems that use the structures or methods described herein. Separate embodiments may also be provided in combination in a single embodiment, and conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Further, reference to values stated in ranges includes each and every value within that range. Many other embodiments may be apparent to skilled artisans only after reading this specification. Other embodiments may be used and

derived from the disclosure, such that a structural substitution, logical substitution, or another change may be made without departing from the scope of the disclosure. Accordingly, the disclosure is to be regarded as illustrative rather than restrictive.

What is claimed is:

1. A lubricating composition comprising:
 - a) a major amount of an oil of lubricating viscosity;
 - b) a non-borated dispersant;
 - c) a borated dispersant in an amount sufficient to provide less than about 160 ppm of boron to the lubricating composition,
wherein the combination of non-borated dispersant and borated dispersant provide at least about 250 ppm of nitrogen to the lubricating composition;
 - d) molybdenum-containing compounds in an amount sufficient to provide at least about 400 ppm of molybdenum to the lubricating composition,
wherein the molybdenum-containing compounds comprises molybdenum dithiocarbamate;
 - e) an overbased calcium salicylate detergent; and
 - f) a viscosity index improver (VII);
wherein the high temperature high shear viscosity at 100 °C (HTHS100) of the lubricating composition between 3.0 mPa·s to 4.5 mPa·s.
2. The lubricating composition of claim 1, wherein the borated dispersant is present in an amount sufficient to provide about 90 ppm to about 160 ppm of boron to the lubricating composition.
3. The lubricating composition of claim 1, wherein the combination of non-borated dispersant and borated dispersant provide about 250 ppm to about 600 ppm of nitrogen to the lubricating composition.
4. The lubricating composition of claim 1, wherein the molybdenum-containing compounds further comprises a molybdenum-amine complex, a molybdenum dithiophosphate, or a combination thereof.
5. The lubricating composition of claim 1, wherein the molybdenum-containing compounds is present in an amount sufficient to provide about 400 ppm to about 1600 ppm of molybdenum to the lubricating composition.
6. The lubricating composition of claim 1, wherein the overbased calcium salicylate detergent is present in an amount sufficient to provide about 800 ppm to about 2000 ppm of calcium to the lubricating composition.
7. The lubricating composition of claim 1, wherein the viscosity index improver (VII) is a linear polymethacrylate (PMA) or a comb-shaped polymethacrylate (PMA).

8. The lubricating composition of claim 1, wherein the viscosity index improver has a shear stability index (SSI) is less than about 30 as measured by ASTM method D6278.
9. The lubricating composition of claim 1, wherein the lubricating composition further comprises a magnesium detergent, wherein the magnesium detergent is present in an amount sufficient to provide about 300 ppm to about 700 ppm of magnesium to the lubricating composition.
10. The lubricating composition of claim 1, wherein the oil of lubricating viscosity is a Group III base oil.
11. The lubricating composition of claim 1, wherein the lubricating composition further comprises a zinc dithiophosphate, wherein the zinc dithiophosphate is present in an amount sufficient to provide about 500 ppm to about 1200 ppm of zinc to the lubricating composition.
12. The lubricating composition of claim 11, wherein the zinc dithiophosphate is a secondary zinc dithiophosphate.
13. A method of improving fuel economy in an internal combustion engine equipped with a roller-follower type valve train, the method comprising lubricating the internal combustion engine with a lubricating composition comprising:
- a) a major amount of an oil of lubricating viscosity;
 - b) a non-borated dispersant;
 - c) a borated dispersant in an amount sufficient to provide less than about 160 ppm of boron to the lubricating composition,
- wherein the combination of non-borated dispersant and borated dispersant provide at least about 250 ppm of nitrogen to the lubricating composition;
- d) molybdenum-containing compounds in an amount sufficient to provide at least about 400 ppm of molybdenum to the lubricating composition,
- wherein the molybdenum-containing compounds comprises molybdenum dithiocarbamate;
- e) an overbased calcium salicylate detergent; and
 - f) a viscosity index improver (VII).
14. The method of claim 13, wherein the high temperature high shear viscosity at 100 °C (HTHS100) of the lubricating composition is between 3.0 mPa·s to 4.5 mPa·s.
15. The method of claim 13, wherein the borated dispersant is present in an amount sufficient to provide about 90 ppm to about 160 ppm of boron to the lubricating composition.

16. The method of claim 13, wherein the combination of non-borated dispersant and borated dispersant provide about 250 ppm to about 600 ppm of nitrogen to the lubricating composition.
17. The method of claim 13, wherein the molybdenum-containing compounds further comprises a molybdenum-amine complex, a molybdenum dithiophosphate, or a combination thereof.
18. The method of claim 13, wherein the molybdenum-containing compounds is present in an amount sufficient to provide about 400 ppm to about 1600 ppm of molybdenum to the lubricating composition.
19. The method of claim 13, wherein the overbased calcium salicylate detergent is present in an amount sufficient to provide about 800 ppm to about 2000 ppm of calcium to the lubricating composition.
20. The method of claim 13, wherein the viscosity index improver (VII) is a linear polymethacrylate (PMA) or a comb-shaped polymethacrylate (PMA).
21. The method of claim 13, wherein the viscosity index improver has a shear stability index (SSI) is less than about 30 as measured by ASTM method D6278.
22. The method of claim 13, wherein the lubricating composition further comprises a magnesium detergent, wherein the magnesium detergent is present in an amount sufficient to provide about 300 ppm to about 700 ppm of magnesium to the lubricating composition.
23. The method of claim 13, wherein the oil of lubricating viscosity is a Group III base oil.
24. The method of claim 13, wherein the lubricating composition further comprises a zinc dithiophosphate, wherein the zinc dithiophosphate is present in an amount sufficient to provide about 500 ppm to about 1200 ppm of zinc to the lubricating composition.
25. The method of claim 24, wherein the zinc dithiophosphate is a secondary zinc dithiophosphate.
26. The method of claim 13, wherein the improvement in fuel economy is measured by the JASO M366 fuel economy test.

27. The method of claim 26, wherein the Fuel Economy Improvement (FEI) as measured by the JASO M366 fuel economy test is greater than 1.10%.

28. The use of a lubricating composition to improve the fuel economy of an internal combustion engine equipped with a roller-follower type valve train, wherein the lubricating composition comprises:

- a) a major amount of an oil of lubricating viscosity;
- b) a non-borated dispersant;
- c) a borated dispersant in an amount sufficient to provide less than about 160 ppm of boron

to the lubricating composition,

wherein the combination of non-borated dispersant and borated dispersant provide at least about 250 ppm of nitrogen to the lubricating composition;

d) molybdenum-containing compounds in an amount sufficient to provide at least about 400 ppm of molybdenum to the lubricating composition,

wherein the molybdenum-containing compounds comprises molybdenum dithiocarbamate;

- e) an overbased calcium salicylate detergent; and
- f) a viscosity index improver (VII).