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(54) **METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE**

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(57) **ABSTRACT**

The disclosed technology provides a method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising: an oil of lubricating viscosity, a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40, an alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9, and a TBN of 81 to 180 mg KOH/g, wherein the sulfonate detergents provide a total amount of sulfonate substrate of 1 wt % to 3 wt % of the lubricating composition, 0.1 to 1.2 wt % of antioxidant, wherein at least 20 wt % of the antioxidant is a phenolic antioxidant, a borated compound present in an amount to deliver 25 ppm to 300 ppm of boron, the lubricating composition has a sulfated ash content of 0.5 wt % to not more than 1.5 wt %, and the lubricating composition has a TBN of 6.5 to 15 mg KOH/g.

## METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE

### CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation application of Ser. No. 15/556,355 filed on Sep. 7, 2017, which is a 371 national phase filing of PCT Application Serial No. PCT/US2016/021206 filed on Mar. 7, 2016, which claims benefit from Provisional Application Ser. No. 62/130,229 filed on Mar. 9, 2015.

### FIELD OF INVENTION

[0002] The disclosed technology provides method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising: an oil of lubricating viscosity, a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40, an alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9, and a TBN of 81 to 180 mg KOH/g, wherein the sulfonate detergents provide a total amount of sulfonate substrate of 1 wt % to 3 wt % of the lubricating composition, 0.1 to 1.2 wt % of antioxidant, wherein at least 20 wt % of the antioxidant is a phenolic antioxidant, a borated compound present in an amount to deliver 25 ppm to 300 ppm of boron, the lubricating composition has a sulfated ash content of 0.5 wt % to not more than 1.5 wt %, and the lubricating composition has a TBN of 6.5 to 15 mg KOH/g.

### BACKGROUND OF THE INVENTION

[0003] Phenol-based detergents are known. Among these are phenates based on phenolic monomers, linked with sulfur bridges or alkylene bridges such as methylene linkages derived from formaldehyde. The phenolic monomers themselves are typically substituted with an aliphatic hydrocarbyl group to provide a measure of oil solubility. The hydrocarbyl groups may be alkyl groups, and, historically, dodecylphenol (or propylene tetramer-substituted phenol) has been widely used. An early reference to basic sulfurized polyvalent metal phenates is U.S. Pat. No. 2,680,96, Walker et al., Jun. 1, 1954; see also U.S. Pat. No. 3,372,116, Meinhardt, Mar. 6, 1968.

[0004] Alkylphenol based detergents are known for efficacy to provide deposit control, antioxidancy, and assisting in reducing wear. However, certain alkylphenols and products prepared from them have come under increased scrutiny due to their association as potential endocrine disruptive materials. In particular, alkylphenol detergents which are based on oligomers of C12 alkyl phenols may contain residual monomeric C12 alkyl phenol species.

[0005] U.S. Pat. No. 7,943,796 (Campbell et al, 4 Feb. 2010) discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound, wherein the alkyl group of the alkylhydroxyaromatic compound is derived from an olefin mixture comprising propylene oligomers having an initial boiling point of at least about 195° C. and a final boiling point of no more than about 325° C. as measured by ASTM D86. Also disclosed is a lubricating oil composition containing at least (a) a major amount of an oil of lubricating viscosity and (b) the overbased salt of the oligomerized alkylhydroxyaromatic compound.

[0006] U.S. Pat. No. 7,435,709 (Stonebaker et al, 1 Mar. 2007) discloses a lubricating oil composition displaying reduced endocrine disruption response, comprising a major amount of an oil of lubricating viscosity; and a detergent comprising an unsulfurized alkali or alkaline earth metal salt of a reaction product of (1) an olefin having at least 10 carbon atoms, wherein greater than 80 mole % of the olefin is a linear C20-C30 n-alpha olefin, wherein less than 10 mole % of the olefin is a linear olefin of less than 20 carbon atoms, and wherein less than 5 mole % of the olefin is branched chain olefin of 18 carbons or less, and (2) a hydroxyaromatic compound.

[0007] U.S. Pat. No. 8,183,192 (Sinquinn et al, 4 Aug. 2011) discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound for use in a lubricating oil composition, wherein the alkyl group of the alkylhydroxyaromatic compound is derived from an olefin mixture comprising propylene oligomers having an initial boiling point of at least about 195° C. and a final boiling point of greater than 325° C. and up to about 400° C. as measured by ASTM D86. Also disclosed is a propylene oligomer having an initial boiling point of at least about 195° C. and a final boiling point of greater than 325° C. and up to about 400° C. as measured by ASTM D86, wherein the propylene oligomer contains a distribution of carbon atoms that comprise at least about 50 weight percent of C14 to C20 carbon atoms.

[0008] U.S. Pat. No. 8,207,380 (Campbell et al., 30 Oct. 2008) discloses an alkylated hydroxyaromatic compound prepared by reacting at least one hydroxyaromatic compound with a branched olefinic oligomer having from about 20 to about 80 carbon atoms in the presence of an acid catalyst. The alkylated hydroxyaromatic compound has been determined to be substantially free of endocrine disruptive chemicals when the effects are quantified on pubertal development and thyroid function in the intact juvenile female rat.

[0009] U.S. Pat. No. 8,198,225 (Harrison et al., 4 Jun. 2009) discloses a sulfurized metal alkyl phenate compositions having a low alkyl phenol content. The sulfurized metal alkyl phenate compositions can be prepared by reacting a phenol compound of Formula (I) disclosed therein with an aldehyde to form a phenolic resin of Formula (II) disclosed therein and then by reacting the phenolic resin simultaneously with a metal base and a first sulfurizing agent. The sulfurized metal alkyl phenate compositions and the overbased sulfurized metal alkyl phenate compositions disclosed therein may be used as detergents for formulating lubricating oil compositions. The lubricating oil compositions disclosed therein have a reduced amount of the free phenol compound and a salt thereof.

[0010] US Patent application 2011/0124539 (Sinquinn et al., 26 May 2011) discloses an overbased, sulfurized salt of at least one alkylated hydroxyaromatic compound, wherein the alkyl substituent of the hydroxyaromatic compound is a residue of at least one isomerized olefin having from about 15 to about 99 wt % branching is disclosed. The overbased, sulfurized salt of at least one alkylated hydroxyaromatic compound is produced by the process comprising: (a) alkylating at least one hydroxyaromatic compound with at least one isomerized olefin having from about 15 to about 99 wt % branching obtained by isomerizing at least one normal alpha olefin having from about 10 to about 40 carbon atoms, to provide at least one alkylated hydroxyaromatic compound; (b) neutralizing and sulfurizing the alkylated hydrox-

aromatic compound in any order to provide at least one neutralized, sulfurized alkylated hydroxyaromatic compound; and (c) overbasing the at least one neutralized, sulfurized alkylated hydroxyaromatic compound

**[0011]** International publication WO 2013/059173A1 (Cook et al, 25 Apr. 2013) discloses a bridged dimeric or oligomeric phenolic compound comprising: at least one monomer unit (a) of phenol or an alkyl-substituted phenol wherein the alkyl group contains 1 to 8 carbon atoms, or mixtures thereof; at least one monomer unit (b) of an aliphatic hydrocarbyl-substituted phenol wherein the aliphatic hydrocarbyl group contains at least about 25 carbon atoms, or mixtures thereof; and at least one sulfur-containing or carbon-containing bridging group; or a salt of said oligomeric material; wherein the average number of carbon atoms in said alkyl groups and said aliphatic hydrocarbyl groups is 10 to 100.

**[0012]** International publication based upon application number WO U.S. Ser. No. 15/010,802, filed 9 Jan. 2015, entitled Method of Lubricating an Internal Combustion engine (with inventors Galic Raguz, Mary, and Loop, John G) discloses a method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising: an oil of lubricating viscosity, a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40, 0.1 wt % to 4 wt % of a borated polyisobutylene succinimide dispersant, wherein the polyisobutylene from which the borated polyisobutylene succinimide is derived has a number average molecular weight of 550 to 1150, and 0.1 wt % to 6 wt % of a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 1550 to 2500, 0 wt % to 0.2 wt % of a phenolic based detergent, wherein the total amount of soap delivered by the alkaline earth metal sulfonate (typically calcium sulfonate) is 0.4 to 1 wt % of the lubricating composition, and wherein the lubricating composition has a sulfated ash content of not more than 1.5 wt %.

**[0013]** International publication based upon application number WO U.S. Ser. No. 15/010,793, filed 9 Jan. 2015, entitled Method of Lubricating an Internal Combustion engine (with inventors Galic Raguz, Mary, and Loop, John G) discloses a method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising: an oil of lubricating viscosity, 1.5 wt % to 10 wt % of an ashless dispersant, a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40, and a 80 TBN or lower alkaline earth metal sulfonate detergent having a metal ratio of 1 to 5, wherein the lubricating composition comprises 0 wt % to 0.2 wt % of a phenolic based detergent, the ratio of higher alkaline earth metal sulfonate detergent to lower alkaline earth metal sulfonate detergent is 80:20 to 20:80, the total amount of soap delivered by the calcium sulfonate detergents is 0.4 wt % to 1.5 wt % of the lubricating composition, and the lubricating composition has a sulfated ash content of not more than 1.5 wt %.

#### SUMMARY OF THE INVENTION

**[0014]** It would be useful for a lubricating composition that may be used in diesel engines that operate under severe

conditions and loads while reducing the impact of soot and soot-related wear as well as cleanliness and deposits. For example the lubricating composition may have at least one of enhanced deposit control, increased wear control (i.e., reduced wear) or copper or lead Pb corrosion control.

**[0015]** The disclosed technology allows for an internal combustion engine (typically a compression ignited engine) to have at least one of reduced soot, reduced deposit formation, reduced wear and improved cleanliness.

**[0016]** As used herein reference to the amounts of additives present in the lubricating composition disclosed herein are quoted on an oil free basis, i.e., amount of actives, unless otherwise indicated.

**[0017]** As used herein, the transitional term “comprising”, which is synonymous with “including”, “containing”, or “characterized by”, is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of”, where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the basic, essential and novel characteristics of the composition or method under consideration.

**[0018]** As used herein the expression “compression ignited internal combustion engine” is intended to encompass internal combustion engines that has at least in part compression ignition. As a result the disclosed technology is intended to encompass a method of lubricating a compression ignited internal combustion engine, as well as spark assisted compression ignited internal combustion engines.

**[0019]** As used herein the term “soap” means the surfactant portion of a detergent and does not include a metal base, such as calcium carbonate. The soap term may also be referred to as a detergent substrate. For example, the sulfonate detergents described herein, the soap or substrate may be a neutral salt of an alkylbenzenesulfonic acid.

**[0020]** As used herein all total base number values cited are determined by ASTM Method D2896-11.

**[0021]** The disclosed technology provides a method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising:

**[0022]** an oil of lubricating viscosity,

**[0023]** a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40,

**[0024]** an alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9, and a TBN of 81 to 180 mg KOH/g (as measured by ASTM D2896-11),

**[0025]** wherein the sulfonate detergents provide a total amount of sulfonate substrate of 0.8 wt % to 3 wt %, or 0.9 wt % to 3 wt %, or 1 wt % to 3 wt % of the lubricating composition,

**[0026]** 0.1 to 1.2 wt % of antioxidant, wherein at least 20 wt % of the antioxidant may be a phenolic antioxidant,

**[0027]** a borated compound present in an amount to deliver 25 ppm to 300 ppm of boron and the borated compound may be chosen from

**[0028]** a borate-ester,

**[0029]** a borated dispersant, and

wherein

the lubricating composition has a sulfated ash content of 0.4 wt % to 2 wt %, or 0.5 wt % to 1.8 wt %, or 0.5 wt % to not more than 1.5 wt %, and

the lubricating composition has a TBN of 6.5 to 15 mg KOH/g (as measured by ASTM D2896-11).

[0030] In one embodiment the disclosed technology relates to a method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising:

[0031] an oil of lubricating viscosity,

[0032] a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40,

[0033] an alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9, and a TBN of 81 to 180 mg KOH/g (as measured by ASTM D2896-11),

[0034] wherein the sulfonate detergents provide a total amount of sulfonate substrate of 0.8 wt % to 3 wt %, or 0.9 wt % to 3 wt %, or 1 wt % to 3 wt % of the lubricating composition,

[0035] a borate-ester present in an amount to deliver 75 ppm to 200 ppm, or 75 ppm to 150 ppm of boron,

[0036] 0.1 to 1.2 wt % of antioxidant, wherein at least 20 wt % of the antioxidant may be a phenolic antioxidant, wherein

[0037] the lubricating composition has a sulfated ash content of 0.4 wt % to 2 wt %, or 0.5 wt % to 1.8 wt %, or 0.5 wt % to not more than 1.5 wt %, and the lubricating composition has a TBN of 6.5 to 15 mg KOH/g (as measured by ASTM D2896-11).

[0038] In one embodiment the disclosed technology relates to method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising:

[0039] an oil of lubricating viscosity,

[0040] a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40,

[0041] an alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9, and a TBN of 81 to 180 mg KOH/g (as measured by ASTM D2896-11),

[0042] wherein the sulfonate detergents provide a total amount of sulfonate substrate of 0.8 wt % to 3 wt %, or 0.9 wt % to 3 wt %, or 1 wt % to 3 wt % of the lubricating composition,

[0043] a borated dispersant present in an amount to deliver 125 ppm to 250 ppm of boron,

[0044] 0.1 to 1.2 wt % of antioxidant, wherein at least 20 wt % of the antioxidant may be a phenolic antioxidant, wherein

[0045] the lubricating composition has a sulfated ash content of 0.4 wt % to 2 wt %, or 0.5 wt % to 1.8 wt %, or 0.5 wt % to not more than 1.5 wt %, and

[0046] the lubricating composition has a TBN of 6.5 to 15 mg KOH/g (as measured by ASTM D2896-11).

[0047] In one embodiment the lubricating composition comprises 0 wt % to 0.2 wt %, or 0 wt % to 0.1 wt % of a phenolic based detergent.

[0048] In a different embodiment the lubricating composition comprises 0.01 wt % to 0.2 wt %, or 0.05 wt % to 0.1 wt % of the phenolic based detergent.

[0049] Typically the lubricating composition comprises 0 wt % of a phenolic based detergent.

[0050] The phenolic based detergent may be a phenate.

[0051] The phenolic based detergent may be chosen from a phenate, and a salicylate.

[0052] The phenolic based detergent may be chosen from a phenate, a salicylate, and a salixarate.

[0053] The phenate may be a non-sulfur containing phenate, sulfur containing phenate, or a "hybrid" detergent formed with mixed surfactant system, wherein the hybrid is a mixed phenate-salicylate, a sulfonate-phenate, or a sulfonate-phenate-salicylate.

[0054] In one embodiment the lubricating composition comprises 0 wt % of the phenolic based detergent. In this embodiment the lubricating composition comprises a detergent package of only sulfonate detergents.

[0055] Typically the sulfonate detergent may be a calcium sulfonate, or magnesium sulfonate. Often the sulfonate may be a calcium sulfonate detergent.

[0056] The total amount of substrate delivered by the calcium sulfonate detergents may be 1.00 to 1.6 wt %, 1.05 to 1.2 wt %, or 1.05 to 1.1 wt % of the lubricating composition.

[0057] The 300 TBN or higher alkaline earth metal sulfonate detergent disclosed herein may have a metal ratio of 10 to 40, or 15 to 30, or 20 to 30, or 22 to 25. The calcium sulfonate detergent may have for instance a metal ratio of 10 to 40 has a TBN of 350 to 500, or 375 to 425, and a metal ratio of 20 to 25. For example, the alkaline earth metal sulfonate detergent may have a TBN of 375 to 425, and a metal ratio of 20 to 30, or 22 to 25.

[0058] The 300 TBN or higher alkaline earth metal sulfonate detergent may be a calcium or magnesium sulfonate detergent, typically a calcium sulfonate detergent.

[0059] The alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9, and a TBN of 81 to 130 mg KOH/g, or 82 to 100 mg KOH/g. The metal ratio may be metal ratio of 4 to 8, or greater than 5 to 8, and the TBN may be 85 to 95 mg KOH/g.

[0060] The alkaline earth metal sulfonate detergent may have a metal ratio of 3 to 9, and be a calcium or magnesium sulfonate detergent, typically a calcium sulfonate detergent.

[0061] In one embodiment the sulfonate detergent having a metal ratio of 3 to 9, and the sulfonate detergent having a metal ratio 10 to 40 are both calcium sulfonate detergents.

[0062] The compression-ignition internal combustion engine may be referred to as a heavy duty diesel engine. The laden mass (sometimes referred to as gross vehicle weight rating (GVWR)) may be over 2,700 kg (or 6,000 USA pounds) 2,900 kg, or over 3,000 kg, or over 3,300 kg, or over 3,500 kg, or over 3,700 kg, or over 3,900 kg (or 8,500 USA pounds). Typically the upper limit on the laden mass or GVWR may be set by national government and may be 10,000 kg, or 9,000 kg, or 8,000 kg, or 7,500 kg. The upper ranges of laden mass may be up to 400,000 kg, or up to 200,000 kg, or up to 60,000 kg, or up to 44,000 kg, or up to 40,000 kg. Typically a laden mass above 120,000 may be for an off-highway vehicle.

[0063] Heavy duty diesel engines are noted to be limited to all motor vehicles with a "technically permissible maximum laden mass" over 3,500 kg, equipped with compression ignition engines or positive ignition natural gas (NG) or LPG engines. In contrast, the European Union indicates that for new light duty vehicles (passenger cars and light commercial vehicles) included within the scope of ACEA testing

section "C" have a "technically permissible maximum laden mass" not exceeding 2610 kg.

**[0064]** There is a distinct difference between passenger car, and heavy duty diesel engines. The difference in size from over 3,500 kg to not more than 2610 kg means that engines of both types will experience significantly different operating conditions such as load, oil temperatures, duty cycle and engine speeds. Heavy duty diesel engines are designed to maximize torque for hauling payloads at maximum fuel economy while passenger car diesels are designed for commuting people and acceleration at maximum fuel economy. The designed purpose of the engine hauling versus commuting results in different hardware designs and resulting stresses imparted to lubricant designed to protect and lubricate the engine. Another distinct design difference is the operating revolution per minute (RPM) that each engine operates at to haul versus commute. A heavy duty diesel engine such as a typical 12-13 litre truck engine would typically not exceed 2200 rpm while a passenger car engine can go up to 4500 rpm.

**[0065]** In one embodiment the internal combustion engine may be a heavy duty diesel compression ignited (or spark assisted compression ignited) internal combustion engine.

**[0066]** In one embodiment the lubricating composition is characterized as having (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulfated ash content of 0.5 wt % to 1.5 wt % or less.

**[0067]** In one embodiment the lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.2 wt % to 0.4 wt % or less, (ii) a phosphorus content of 0.08 wt % to 0.15 wt %, and (iii) a sulfated ash content of 0.5 wt % to 1.5 wt % or less.

**[0068]** In one embodiment the lubricating composition may be characterized as having a sulfated ash content of 0.9 wt % to 1.4 wt %, or 1.05 wt % to 1.2 wt %.

**[0069]** In one embodiment the lubricating composition comprises an antioxidant, wherein the phenolic antioxidant comprises at least 40 wt %, or at least 50 wt % of the antioxidant, typically 45 wt % to 90 wt %, or 55 wt % to 80 wt % of the antioxidant.

**[0070]** In one embodiment the lubricating composition comprises an aminic antioxidant, typically diarylamine or alkylated diarylamine and include a phenyl- $\alpha$ -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenyl-naphthylamine, or mixtures thereof.

**[0071]** When present the aminic antioxidant comprises at most 60 wt %, or at most 50 wt % of the antioxidant, typically 5 wt % to 55 wt %, or 10 to 45 wt % of the antioxidant.

**[0072]** In one embodiment the lubricating composition comprises a sulfurized olefin such as a sulfurized 4-carbobutoxy cyclohexene, or a sulfurized alpha-olefin (such as C10-24, C14-20, C16-18 alpha-olefins), or sulfurized diisobutylene, or mixtures thereof. When present, the sulfurized olefin antioxidant comprises at most 60 wt %, or at most 50 wt % of the antioxidant, typically 5 wt % to 55 wt %, or 10 to 45 wt % of the antioxidant.

**[0073]** In one embodiment the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof, and wherein the antioxidant may be present at 0.1 wt % to 3 wt %, or 0.5 wt % to 2.75 wt %, or 1 wt % to 2.5 wt %.

**[0074]** The lubricating composition disclosed herein may be characterized as having a total base number (TBN) content of 7 to 14, or 7.5 to 12 mg KOH/g, or 8 to 10 mg KOH/g.

**[0075]** In another embodiment the disclosed technology provides for the use of a lubricating composition disclosed herein to provide at least one of reduced soot, reduced deposit formation, reduced wear and improved cleanliness in a compression ignited internal combustion engine (typically a diesel internal combustion engine).

#### DETAILED DESCRIPTION OF THE INVENTION

**[0076]** The disclosed technology provides a method for lubricating an internal combustion engine and a use as disclosed above.

#### Oils of Lubricating Viscosity

**[0077]** The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

**[0078]** Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

**[0079]** 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. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

**[0080]** Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

**[0081]** Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

**[0082]** Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof.

**[0083]** Other synthetic lubricating oils include polyol esters (such as Priolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, tri-octyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

**[0084]** Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content  $>0.03$  wt %, and/or  $<90$  wt % saturates, viscosity index 80-120); Group II (sulfur content  $\leq 0.03$  wt %, and  $\geq 90$  wt % saturates, viscosity index 80-120); Group III (sulfur content  $\leq 0.03$  wt %, and  $\geq 90$  wt % saturates, viscosity index  $\geq 120$ ); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV).

**[0085]** The oil of lubricating viscosity may also be an API Group II+ base oil, which term refers to a Group II base oil having a viscosity index greater than or equal to 110 and less than 120, as described in SAE publication "Design Practice: Passenger Car Automatic Transmissions", fourth Edition, AE-29, 2012, page 12-9, as well as in U.S. Pat. No. 8,216,448, column 1 line 57.

**[0086]** The oil of lubricating viscosity may also be an API Group III+ base oil, which term refers to a Group III+ base oil having a viscosity index greater than or equal to 130. Group III+ are known in the art and is described in "Lube Report", dated Feb. 26, 2014 in an article entitled "SK Sees Group III Shortfall", by Nancy DeMarco. The article may be obtained from [http://www.aselube.com/media/11910/sk\\_sees\\_group\\_iii\\_shortfall.pdf](http://www.aselube.com/media/11910/sk_sees_group_iii_shortfall.pdf).

**[0087]** The oil of lubricating viscosity may be an API Group IV oil, or mixtures thereof, i.e., a polyalphaolefin. The polyalphaolefin may be prepared by metallocene catalyzed processes or from a non-metallocene process.

**[0088]** The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof.

**[0089]** The oil of lubricating viscosity may comprises an API Group I, Group II, Group III, Group IV oil or mixtures thereof.

**[0090]** The oil of lubricating viscosity may comprises an API Group I, Group II, Group III oil or mixtures thereof.

**[0091]** The oil of lubricating viscosity may comprises an API Group I, Group II oil or mixtures thereof.

**[0092]** The oil of lubricating viscosity may comprises an API Group I oil.

**[0093]** The oil of lubricating viscosity may comprises an API Group II oil.

**[0094]** The amount of the oil of lubricating viscosity present may be typically the balance remaining after subtracting from 100 wt % the sum of the amount of the additive as described herein above, and the other performance additives.

**[0095]** The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the disclosed technology is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of components of the disclosed technology to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

**[0096]** In one embodiment the lubricating composition may be not an aqueous composition.

**[0097]** The lubricating composition comprising may have a kinematic viscosity of 2 cSt to 20 cSt (or  $\text{mm}^2/\text{s}$ ) at 100°

C., as measured by ASTM D445-14. The lubricating composition may be liquid, i.e., not a gel or semi-solid, at ambient temperatures (5-30° C.).

#### Antioxidant

**[0098]** The lubricating composition comprises an antioxidant as described herein. Typically the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof. The antioxidants include diarylamines, alkylated diarylamines, hindered phenols, or mixtures thereof.

**[0099]** The diarylamine or alkylated diarylamine may be a phenyl- $\alpha$ -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenyl-naphthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In another embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include octyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenyl-naphthylamines.

**[0100]** The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in U.S. Pat. No. 6,559,105.

**[0101]** In one embodiment the antioxidant comprises a mixture of a sulfurized olefin, a phenolic, and aminic antioxidant.

**[0102]** For example the antioxidant mixture may be:

phenolic antioxidant comprises at least 40 wt %, or at least 50 wt % of the antioxidant, typically 45 wt % to 90 wt %, or 55 wt % to 80 wt % of the antioxidant;

aminic antioxidant comprises at most 60 wt %, or at most 50 wt % of the antioxidant, typically 5 wt % to 55 wt %, or 10 to 45 wt % of the antioxidant; and

sulfurized olefin antioxidant comprises at most 60 wt %, or at most 50 wt % of the antioxidant, typically 5 wt % to 55 wt %, or 10 to 45 wt % of the antioxidant.

**[0103]** Alternatively, the antioxidant mixture may be:

phenolic antioxidant comprises at least 40 wt %, or at least 50 wt % of the antioxidant, typically 45 wt % to 90 wt %, or 55 wt % to 80 wt % of the antioxidant;

aminic antioxidant comprises at most 60 wt %, or at most 50 wt % of the antioxidant, typically 5 wt % to 55 wt %, or 10 to 45 wt % of the antioxidant; and

sulfurized olefin antioxidant comprises at most 60 wt %, or at most 50 wt % of the antioxidant, typically 5 wt % to 55 wt %, or 10 to 45 wt % of the antioxidant.

## Sulfonate Detergents

**[0104]** The sulfonate detergent of the disclosed technology may be overbased for a detergent having a TBN of at least 300, and neutral to slightly overbased for a TBN of 81 to 130 mg KOH/g as is defined herein.

**[0105]** Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by a metal content in of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a calcium chloride, acetic acid, phenol or alcohol. The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of "excess" metal (stoichiometrically) is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 3.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

**[0106]** The "soap content", metal ratio and TBN are known to a person skilled in the art and explained in standard textbook entitled "Chemistry and Technology of Lubricants", Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, pages 219 to 220 under the sub-heading 7.2.5. Detergent Classification.

**[0107]** The lubricating composition disclosed herein typically comprises at least one calcium sulfonate detergent described herein.

**[0108]** In a different embodiment the lubricating composition comprises at least one or at least two other sulfonate detergents. The sulfonate detergents of the disclosed technology are known to a person skilled in the art.

**[0109]** In another embodiment the lubricating composition further comprises another sulfonate detergent, typically a magnesium, sodium or zinc overbased sulfonate. Typically any additional sulfonate detergent may be a magnesium or sodium sulfonate detergent, with magnesium sulfonate the more typical.

**[0110]** In one embodiment the lubricating composition comprises a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 10 to 40, and a 82 to v100 TBN or lower alkaline earth metal sulfonate detergent having a metal ratio of 3 to 9.

**[0111]** In one embodiment the lubricating composition comprises a 300 TBN or higher alkaline earth metal sulfonate detergent comprises a magnesium sulfonate detergent having a metal ratio of 10 to 40, and a 80 TBN or lower alkaline earth metal sulfonate detergent comprising a calcium sulfonate detergent having a metal ratio of 1 to 5.

**[0112]** In one embodiment the lubricating composition comprises a 300 TBN or higher alkaline earth metal sulfonate detergent comprising a mixture of a calcium sulfonate detergent having a metal ratio of 10 to 40, and a magnesium sulfonate detergent having a metal ratio of 10 to

40, and a 80 TBN or lower alkaline earth metal sulfonate detergent comprises a calcium sulfonate detergent having a metal ratio of 1 to 5.

**[0113]** The 300 TBN or higher alkaline earth metal sulfonate detergent and the 80 TBN or lower alkaline earth metal sulfonate detergent may be prepared from the same or different hydrocarbyl-substituted sulfonic acids. Typically the hydrocarbyl-substituted sulfonic acids are alkyl-substituted sulfonic acids.

**[0114]** The sulfonate may be prepared from a mono- or di-hydrocarbyl-substituted benzene (or toluene, naphthalene, indenyl, indanyl, or bicyclopentadienyl) sulfonic acid, wherein the hydrocarbyl group may contain 6 to 40, or 8 to 35 or 9 to 30 carbon atoms.

**[0115]** The hydrocarbyl group may be derived from polypropylene or a linear or branched alkyl group containing at least 10 carbon atoms. Examples of a suitable alkyl group include branched and/or linear decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonadecyl, eicosyl, un-eicosyl, do-eicosyl, tri-eicosyl, tetra-eicosyl, penta-eicosyl, hexa-eicosyl or mixtures thereof.

**[0116]** In one embodiment the hydrocarbyl-substituted sulfonic acid may include polypropene benzenesulfonic acid and C<sub>16</sub>-C<sub>24</sub> alkyl benzenesulfonic acid, or mixtures thereof.

**[0117]** In one embodiment the 300 TBN sulfonate detergent may be a predominantly linear alkylbenzene sulfonate detergent having a metal ratio of having a metal ratio of 10 to 40 as is described in paragraphs [0026] to [0037] of US Patent Application 2005065045 (and granted as U.S. Pat. No. 7,407,919). The predominantly linear alkylbenzene sulfonate detergent may be particularly useful for assisting in improving fuel economy.

**[0118]** Typically the 300 TBN or higher alkaline earth metal sulfonate detergent has a metal ratio of 12 to 30, or 12 to 22, or 16 to 20, or 10 to 20, or 20 to 30, or 22 to 25 mg KOH/g. In one embodiment the 300 TBN metal ratio may be 16 to 20, and in another embodiment 22 to 25.

**[0119]** In one embodiment the lubricating composition comprises a calcium sulfonate detergent having a metal ratio of 10 to 40, and a calcium sulfonate detergent having a metal ratio of 3 to 9.

**[0120]** In one embodiment the lubricating composition comprises a calcium sulfonate detergent having a metal ratio of 10 to 40, a calcium sulfonate detergent having a metal ratio of 3 to 9, and a magnesium sulfonate detergent having a metal ratio of 12 to 40.

**[0121]** The magnesium sulfonate detergent may have a TBN of 300 to 500, or 350 to 425 mg KOH/g; and a metal ratio of 12 to 40, or 14 to 25. The magnesium sulfonate may have the same or different hydrocarbyl-substituted sulfonic acids, and are defined the same as described above for calcium sulfonate detergents.

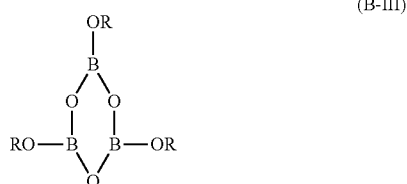
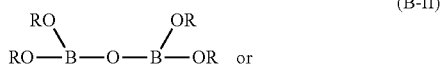
**[0122]** If present the other sulfonate (typically magnesium sulfonate) detergent may be present in an amount such as 0.01 wt % to 0.5 wt %, or 0.2 wt % to 0.3 wt %. Typically the lubricating composition consists of only two (or three) detergents i.e., the two calcium sulfonate detergents, and optionally a magnesium sulfonate detergent which may be present or absent in different embodiments.

## Borated Compound

**[0123]** The borated compound may be present in an amount to deliver 25 ppm to 300 ppm of boron and the

borated compound may be chosen from a borate-ester, a borated dispersant, or mixtures thereof.

[0124] In one embodiment the boron-containing compound may be borate ester represented by the formula:



wherein each R may be independently an organic group and any two adjacent R groups may together form a cyclic group, or wherein the boron-containing compound may be borate ester represented by the formula:

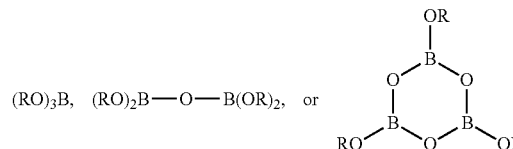
said alkyl group having a branch at the  $\beta$  or higher position, said borate ester being present in an amount to provide 1 to 1000 parts per million by weight of boron to the lubricant composition. Typically the borate ester comprises multiple alkyl groups each independently having 10 to 32 carbon atoms, said alkyl groups having a branch at the  $\beta$  or higher position.

[0127] The alkyl group may be branched at the  $\beta$  position. The alkyl group may have a structure represented by  $-\text{CH}_2-\text{CH}(\text{R}^1)(\text{R}^2)$ , where  $\text{R}^1$  may be an alkyl group of 7 to 18 carbon atoms and  $\text{R}^2$  may be an alkyl group having fewer carbon atoms than  $\text{R}^1$ .

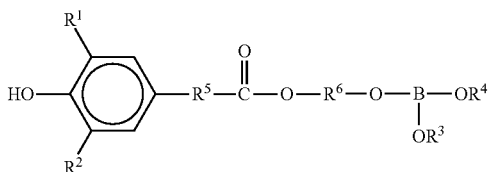
[0128] In one embodiment the alkyl group has a structure represented by  $-\text{CH}_2-\text{CH}(\text{R}^1)(\text{R}^2)$ , where  $\text{R}^1$  may be an alkyl group of 7 to 18 carbon atoms and  $\text{R}^2$  may be an alkyl group having two fewer carbon atoms than  $\text{R}^1$ .

[0129] The alkyl group may be derived from a Guerbet alcohol. The alkyl group may be a 2-propylheptyl group, a 2-butyloctyl group, a 2-hexyldecyl group, or a 2-octyldecyl group.

[0130] In one embodiment the borate ester may be represented by one or more of the formulae:

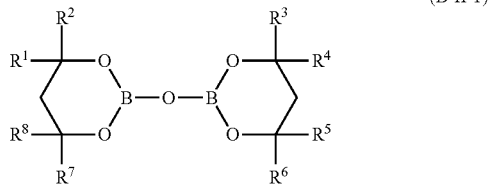


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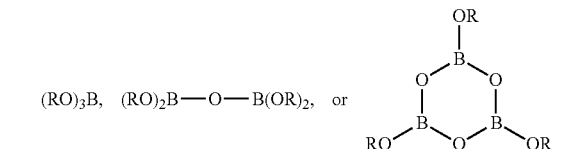
wherein:  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently hydrocarbyl groups of 1 to 12 carbon atoms; and  $\text{R}^5$  and  $\text{R}^6$  are independently alkylene groups of 1 to 6 carbon atoms, and in one embodiment 2 to 4 carbon atoms, where each R may be independently an organic group and any two adjacent R groups may together form a cyclic group.

[0125] In one embodiment the boron-containing compound may be a borate ester represented by the formula:

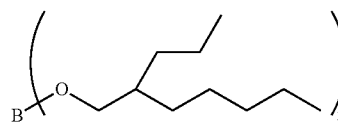


wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  are independently hydrogen or hydrocarbyl groups. Typically each of the hydrocarbyl groups may contain from 1 to 12, or 1 to 4 carbon atoms.

[0126] In one embodiment the borate ester comprises at least one alkyl group having 10 to about 32 carbon atoms,



[0131] The borate ester may comprise a trialkylborate. the borate ester may be a material represented by the structure:



[0132] The borate ester may be present at 75 ppm to 120 ppm, or 80 ppm to 110 ppm of the lubricating composition.

[0133] In one embodiment the borated compound may be a borated dispersant. Typically the borated dispersant may be a borated succinimide. The borated succinimide, or mixtures thereof.

[0134] The borated succinimide may be known to the skilled person and may be prepared by reacting a borating agent such as boric acid, with a polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic succinimide may be derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500.

[0135] The borated polyisobutylene succinimide may have a carbonyl to nitrogen ratio of 1:1 to 1:5, or 1:1 to 1:4, or 1:1.3 to 3: or 1:1.5 to 1:2, or 1:1.4 to 1:0.6.

[0136] The borated dispersant may be present at 125 ppm to 250 ppm, or 150 ppm to 200 ppm of the lubricating composition.



## Non-Borated Dispersant

**[0137]** The lubricating composition may further comprise a non-borated dispersant.

**[0138]** When present the non-borated dispersant may be present at 1 wt % to 8 wt %, or 2.5 wt % to 7 wt %, or 3 wt % to 6 wt % of the lubricating composition.

**[0139]** The non-borated dispersant may typically be a succinimide dispersant.

**[0140]** The non-borated succinimide dispersant may be derived from polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide may be derived has a number average molecular weight of 350 to 5000, or 750 to 3000 or 1550 to 2500.

**[0141]** The non-borated dispersant of both polyisobutylene succinimide may be derived from an aliphatic polyamine, or mixtures thereof.

**[0142]** The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be chosen from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, polyamine still bottoms, and mixtures thereof.

**[0143]** Non-borated polyisobutylene succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. Nos. 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, 7,238,650 and EP Patent Application 0 355 895 A.

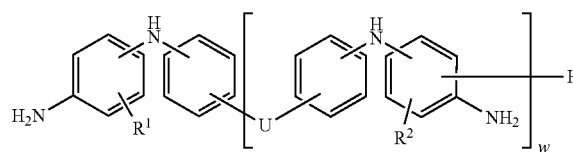
**[0144]** In one embodiment the non-borated the polyisobutylene succinimide may be present at 2.5 wt % to 6 wt %, or 3 wt % to 5 wt % of the lubricating composition.

**[0145]** The non-borated polyisobutylene succinimide may have a carbonyl to nitrogen ratio of 1:1 to 1:5, or 1:1 to 1:4, or 1:1.3 to 3: or 1:1.5 to 1:2, or 1:1.4 to 1:0.6.

**[0146]** In one embodiment the non-borated dispersant may include an amine-functionalized additive may be derived from an amine having at least 3 or 4 aromatic groups.

**[0147]** As used herein the term “an aromatic group” is used in the ordinary sense of the term and is known to be defined by Hückel theory of  $4n+2$   $\pi$  electrons per ring system. Accordingly, one aromatic group may have 6, or 10, or 14  $\pi$  electrons. Hence a benzene ring has 6  $\pi$  electrons,

a naphthylene ring has 10  $\pi$  electrons and an acridine group has 14  $\pi$  electrons. An example of the amine having at least 3 or 4 aromatic groups may be represented by Formula (1):



wherein independently each variable,

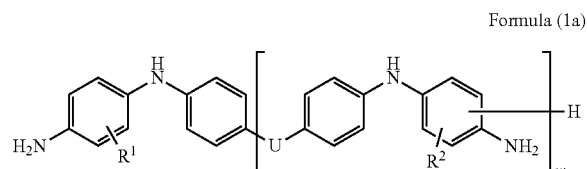
R<sup>1</sup> may be hydrogen or a C<sub>1-5</sub> alkyl group (typically hydrogen);

R<sup>2</sup> may be hydrogen or a C<sub>1-5</sub> alkyl group (typically hydrogen);

U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U may be aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and

w may be 1 to 10, or 1 to 4, or 1 to 2 (typically 1).

**[0148]** An example of the amine having at least 3 or 4 aromatic groups may be represented by Formula (1a):



Formula (1a)

wherein independently each variable,

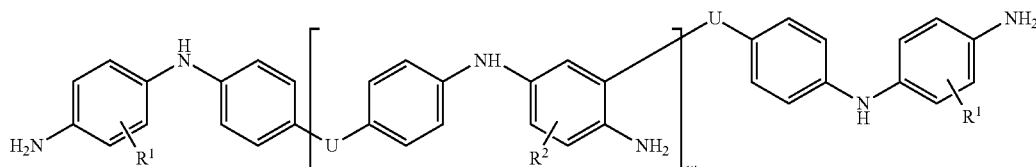
R<sup>1</sup> may be hydrogen or a C<sub>1-5</sub> alkyl group (typically hydrogen);

R<sup>2</sup> may be hydrogen or a C<sub>1-5</sub> alkyl group (typically hydrogen);

U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U may be aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and

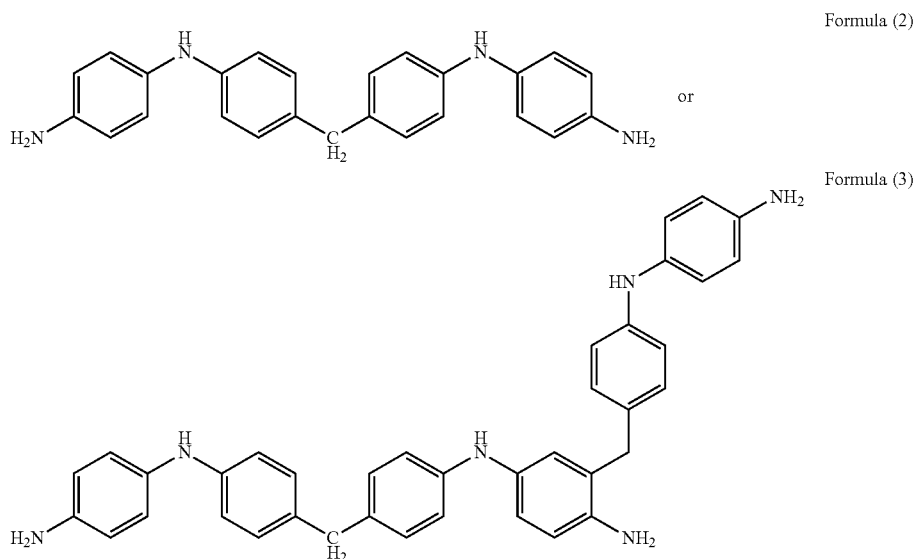
w may be 1 to 10, or 1 to 4, or 1 to 2 (typically 1).

**[0149]** Alternatively, the compound of Formula (1a) may also be represented by:



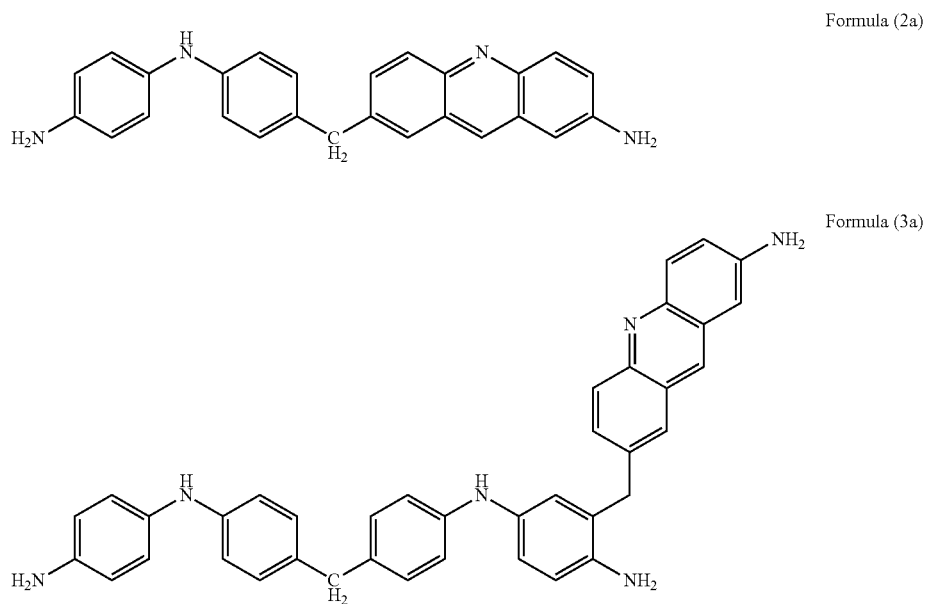
wherein each variable U, l<sub>e</sub>, and R<sup>2</sup> are the same as described above and w may be 0 to 9 or 0 to 3 or 0 to 1 (typically 0).

[0150] Examples of an amine having at least 3 or 4 aromatic groups may be represented by any of the following Formulae (2) and/or (3):

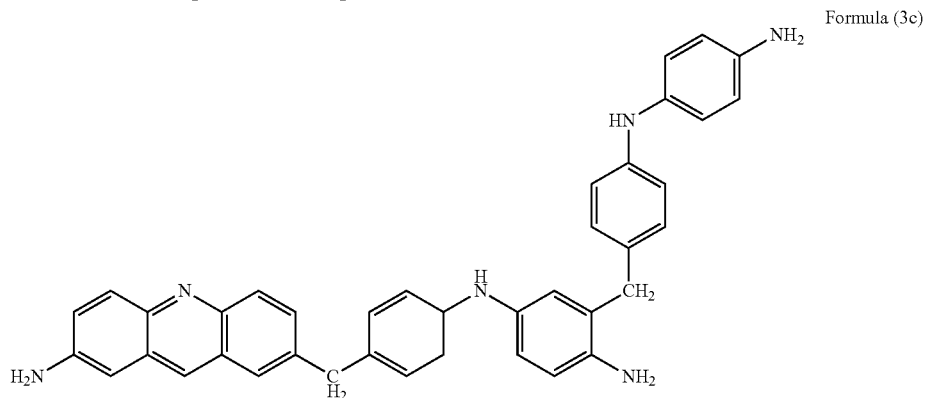
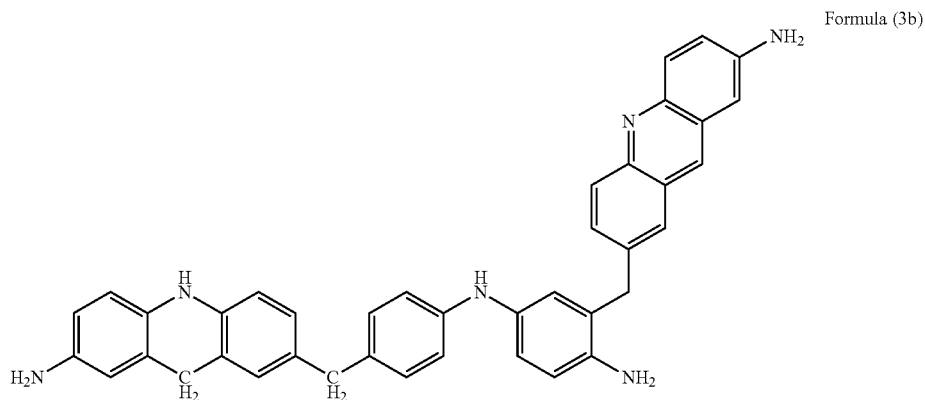


[0151] In one embodiment the amine having at least 3 or 4 aromatic groups may include mixtures of compounds represented by the formulae disclosed above. A person skilled in the art will appreciate that compounds of Formulae (2) and (3) may also react with the aldehyde described below to form acridine derivatives. Acridine derivatives that may be formed include compounds illustrated represented by

Formula (2a) or (3a) to (3c) below. In addition to these compounds represented these formulae, a person skilled in the art will also appreciate that other acridine structures may be possible where the aldehyde reacts with other with benzyl groups bridged with the >NH group. Examples of acridine structures include those represented by Formulae (2a), (3a) or (3b) or (3c):



**[0152]** Any or all of the N-bridged aromatic rings are capable of such further condensation and perhaps aromatisation. One other of many possible structures include Formula (3b):



**[0153]** Any of the formulae above (2), (2a) (3), or (3a) to (3c) could also have further condensation reactions occurring resulting in one or more acridine moieties forming per molecule.

**[0154]** Examples of the amine having at least 3 or 4 aromatic groups may be bis[p-(p-aminoanilino)phenyl]-methane, 2-(7-amino-acridin-2-ylmethyl)-N-4-{4-[4-(4-amino-phenylamino)-benzyl]-phenyl}-benzene-1,4-diamine, N-4-{4-[4-(4-amino-phenylamino)-benzyl]-phenyl}-2-[4-(4-amino-phenylamino)-cyclohexa-1,5-dienylmethyl]-benzene-1,4-diamine, N-[4-(7-amino-acridin-2-ylmethyl)-phenyl]-benzene-1,4-diamine, or mixtures thereof.

**[0155]** In one embodiment the amine having at least 3 or 4 aromatic groups may be bis[p-(p-aminoanilino)phenyl]-methane, 2-(7-amino-acridin-2-ylmethyl)-N-4-{4-[4-(4-amino-phenylamino)-benzyl]-phenyl}-benzene-1,4-diamine or mixtures thereof.

**[0156]** The amine having at least 3 or 4 aromatic groups may be prepared by a process comprising reacting an aldehyde with an amine (typically 4 aminodiphenylamine). The resultant amine may be described as an alkylene coupled amine having at least 3 or 4 aromatic groups, at least one —NH<sub>2</sub> functional group, and at least 2 secondary or tertiary amino groups.

**[0157]** The aldehyde may be aliphatic, alicyclic or aromatic. The aliphatic aldehyde may be linear or branched. Examples of a suitable aromatic aldehyde include benzaldehyde or o-vanillin. Examples of an aliphatic aldehyde

include formaldehyde (or a reactive equivalent thereof such as formalin or paraformaldehyde), ethanal or propanal. Typically the aldehyde may be formaldehyde or benzaldehyde.

**[0158]** Alternatively, the amine having at least 3 or 4 aromatic groups may also be prepared by the methodology described in *Berichte der Deutschen Chemischen Gesellschaft* (1910), 43, 728-39.

**[0159]** In one embodiment the amine having at least 3 or 4 aromatic groups may be obtained/obtainable by a process comprising reacting isatoic anhydride or alkyl substituted isatoic anhydride, with an aromatic amine with at least two aromatic groups and a reactive primary or secondary amino group. The resultant material may be described as an anthranilic derivative.

**[0160]** In one embodiment the anthranilic derivative may be prepared in a reaction containing isatoic anhydride or alkyl substituted isatoic anhydride and an aromatic amine selected from the group consisting of xylylenediamine, 4-aminodiphenylamine, 1,4-dimethylphenylenediamine, and mixtures thereof. In one embodiment the aromatic amine may be 4-aminodiphenylamine.

**[0161]** The process described above to prepare the anthranilic derivative may be carried out at a reaction temperature in the range of 20° C. to 180° C., or 40° C. to 110° C. The process may or may not be carried out in the presence of a

solvent. Examples of a suitable solvent include water, diluent oil, benzene, t-butyl benzene, toluene, xylene, chlorobenzene, hexane, tetrahydrofuran, or mixtures thereof. The reactions may be performed in either air or an inert atmosphere. Examples of suitable inert atmosphere include nitrogen or argon, typically nitrogen.

#### Carboxylic Functionalized Polymer

**[0162]** The amine-functionalized additive may be the reaction product of the amine having at least 3 or 4 aromatic groups with a carboxylic functionalized polymer. The resultant product obtained may be described as being an amine-functionalized carboxylic functionalized polymer.

**[0163]** The carboxylic functionalized polymer backbone may be a homopolymer or a copolymer, provided that it contains at least one carboxylic acid functionality or a reactive equivalent of carboxylic acid functionality (e.g., anhydride or ester). The carboxylic functionalized polymer may have a carboxylic acid functionality (or a reactive equivalent of carboxylic acid functionality) grafted onto the backbone, within the polymer backbone or as a terminal group on the polymer backbone.

**[0164]** The carboxylic functionalized polymer may be a polyisobutylene-succinic anhydride, a maleic anhydride-styrene copolymer, an ester of a maleic anhydride-styrene copolymer, an alpha olefin-maleic anhydride copolymer, or a maleic anhydride graft copolymer of (i) a styrene-ethylene-alpha olefin polymer, (ii) a hydrogenated alkenyl aryl conjugated diene copolymer ((that is, a hydrogenated alkenyl arene conjugated diene copolymer, in particular a hydrogenated copolymer of styrene-butadiene), (iii) a polyolefin grafted with maleic anhydride (in particular ethylene-propylene copolymer), or (iv) a isoprene polymer (in particular non-hydrogenated isobutylene-isoprene copolymer or a hydrogenated styrene-isoprene polymer), or mixtures thereof.

**[0165]** The carboxylic functionalized polymer described herein is known in lubricant technology. For example:

**[0166]** (i) esters of maleic anhydride and styrene-containing polymers are known from U.S. Pat. No. 6,544,935;

**[0167]** (ii) grafted styrene-ethylene-alpha olefin polymers are taught in International publication WO 01/30947;

**[0168]** (iii) copolymers derived from isobutylene and isoprene have been used in preparing dispersants and are reported in International publication WO 01/98387;

**[0169]** (iv) grafted styrene-butadiene and styrene-isoprene copolymers are described in a number of references including DE 3,106,959; and U.S. Pat. Nos. 5,512,192, and 5,429,758;

**[0170]** (v) polyisobutylene succinic anhydrides have been described in numerous publications including U.S. Pat. Nos. 4,234,435; 3,172,892; 3,215,707; 3,361,673; and 3,401,118;

**[0171]** (vi) grafted ethylene-propylene copolymers have been described in U.S. Pat. No. 4,632,769; 4,517,104; and 4,780,228;

**[0172]** (vii) esters of (alpha-olefin maleic anhydride) copolymers have been described in U.S. Pat. No. 5,670,462;

**[0173]** (viii) copolymers of isobutylene and conjugated dienes (such as isobutylene-isoprene copolymer) have

been described in U.S. Pat. Nos. 7,067,594 and 7,067,594 and US Patent Application US 2007/0293409; and

terpolymers of ethylene, propylene and non-conjugated diene (such as dicyclopentadiene or butadiene) and described in U.S. Pat. Nos. 5,798,420 and 5,538,651.

**[0174]** Typically the polymers mentioned in (iii), (iv) and (viii) that contain dienes e.g., butadiene or isoprene) are partially or wholly hydrogenated.

**[0175]** Many of the polymer backbones are also described in "Chemistry and Technology of Lubricants, Second Edition, Edited by R. M. Mortier and S. T. Orszulik Published by Blackie Academic & Professional. In particular pages 144-180 discuss many of the polymer backbones (i)-(iv) and (vi)-(viii).

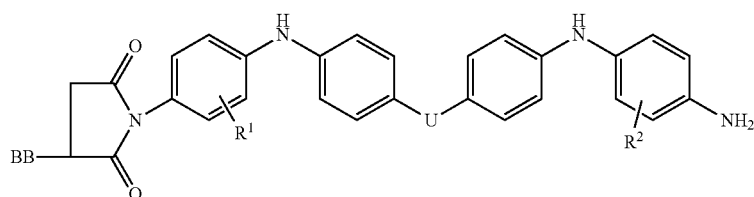
**[0176]** The polymer backbone (other than a polyisobutylene) of the disclosed technology may have a number average molecular weight (by gel permeation chromatography, polystyrene standard), which may be up to 150,000 or higher, e.g., 1,000 or 5,000 to 150,000 or to 120,000 or to 100,000. An example of a suitable number average molecular weight range includes 10,000 to 50,000, or 6,000 to 15,000, or 30,000 to 50,000. In one embodiment, the polymer backbone has a number average molecular weight of greater than 5,000, for instance, greater than 5000 to 150,000. Other combinations of the above-identified molecular weight limitations are also contemplated.

**[0177]** When the polymer backbone is a polyisobutylene, its number average molecular weight (by gel permeation chromatography, polystyrene standard), may be 350 to 5000, or 550 to 3000 or 750 to 2500. (Thus, a polyisobutylene succinic anhydride may be derived from a polyisobutylene with any of the foregoing molecular weights.) Commercially available polyisobutylene polymers have a number average molecular weight of 550, 750, 950-1000, 1550, 2000, or 2250. Some of the commercially available polyisobutylene polymers may obtain the number average molecular weights shown above by blending one or more polyisobutylene polymers of different weights.

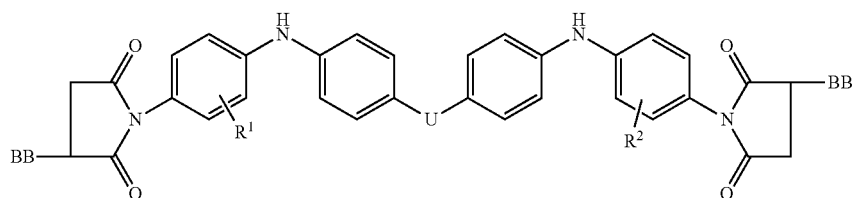
**[0178]** In one embodiment the product may be obtained/obtainable by reacting a carboxylic functionalized polymer with an amine-functionalized additive having at least 3 or 4 aromatic groups, at least one  $\text{—NH}_2$  functional group, and at least 2 secondary or tertiary amino groups.

**[0179]** The amine-functionalized additive having at least 3 or 4 aromatic groups may be reacted with the carboxylic functionalized polymer under known reaction conditions. The reaction conditions are known to a person skilled in the art for forming imides and/or amides of carboxylic functionalized polymers.

**[0180]** The amine-functionalized carboxylic functionalized polymer obtained/obtainable by reacting a carboxylic functionalized polymer with an amine having at least 3 or 4 aromatic groups, at least one  $\text{—NH}_2$  functional group, and at least 2 secondary or tertiary amino groups may in certain embodiment be represented by the Formulae (4) and/or (5):



Formula (4)



Formula (5)

wherein independently each variable,  
R<sup>1</sup>, R<sup>2</sup> and U are described previously;

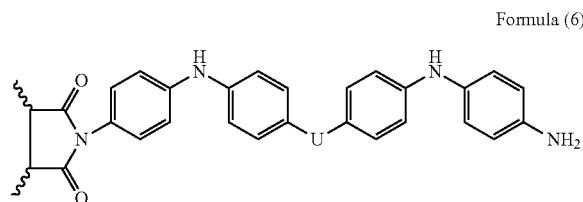
BB may be a polymer backbone and may be polyisobutylene, or copolymers of (i) hydrogenated alkenyl aryl conjugated diene copolymers (in particular hydrogenated copolymers of styrene-butadiene), (ii) polyolefins (in particular ethylene-alphaolefins such as ethylene-propylene copolymers), (iii) hydrogenated isoprene polymers (in particular hydrogenated styrene-isoprene polymers), or (iv) a copolymer of isoprene and isobutylene. BB may be substituted with one succinimide group as is shown in formulae (4) and (5), or it may be substituted by multiple succinimide groups. In one embodiment BB may be a copolymer of isoprene and isobutylene.

**[0181]** In addition to formulae (4) and (5), additional structures may also be formed including trimers, tetramers, higher-mers or mixtures thereof. The amino groups shown in Formulae (4) and (5) may also be replaced, in whole, or in part, by the amine of formulae (2a), (3), (3a), or mixtures thereof.

**[0182]** When BB may be polyisobutylene the resultant carboxylic functionalized polymer may typically be polyisobutylene succinic anhydride. Typically w, as defined in Formula (1) may be 1 to 5, or 1 to 3.

**[0183]** When BB may be other than polyisobutylene, and has maleic anhydride (or other carboxylic acid functionality) grafted thereon, one or more of the grafted maleic anhydride groups may be a succinimide of the amine upon reaction with the amine. The number of succinimide groups may be 1 to 40, or 2 to 40, or 3 to 20.

**[0184]** The amine-functionalized carboxylic functionalized polymer may be obtained/obtainable by reacting a carboxylic functionalized polymer derived from maleic anhydride-styrene copolymers, esters of maleic anhydride-styrene copolymers, alpha-olefin maleic anhydride copolymers; or mixtures thereof with an amine having at least 3 or 4 aromatic groups, at least one —NH<sub>2</sub> functional group, and at least 2 secondary or tertiary amino groups. Typically the product of this type may be described as an alternating copolymer. Within the alternating copolymer one or more of the maleic anhydride derived groups may have a group represented by Formula (6):



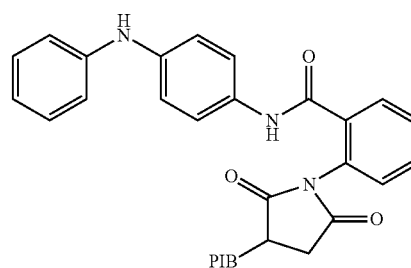
Formula (6)

wherein R<sup>1</sup>, R<sup>2</sup> and U are described previously, and the group of Formula (6) may be bonded to components of the polymer backbone through one or both wavy bonds as shown on the maleic ring structure above. When only one wavy bond is bonded to the polymer, the second wavy bond may be to a hydrogen.

**[0185]** The amine containing group in formula (6) may also be replaced by the amine in formula (3), or mixtures thereof.

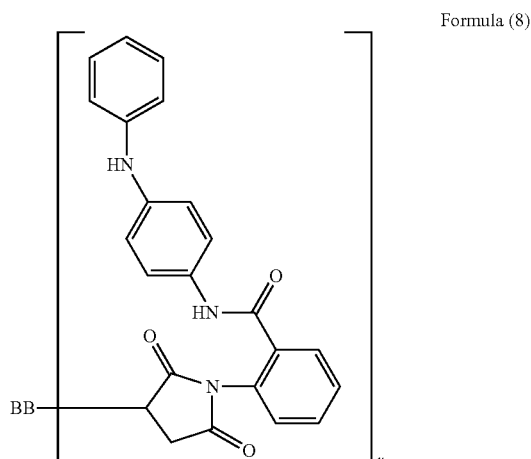
**[0186]** In one embodiment the amine-functionalized carboxylic functionalized polymer may be derived from a polyisobutylene polymer backbone (represented by PIB in formula 7 below). A more detailed description of the polyisobutylene polymer backbone is described previously in the description.

**[0187]** An example of suitable structures of the anthranilic derivative derived from polyisobutylene, the anthranilic derivative and 4-aminodiphenylamine may be represented by Formula (7):



Formula (7)

**[0188]** In one embodiment the amine-functionalized carboxylic functionalized polymer may be derived from one of the aromatic amines and from a non-polyisobutylene polymer backbone. Examples of suitable structures of the anthranilic derivative derived from 4-aminodiphenylamine may be represented by Formula (8):



wherein BB may be a polymer (typically BB may be an ethylene-propylene copolymer derived from ethylene-propylene copolymers). As shown BB is grafted with maleic anhydride and functionalized to form the imide group, and u may be the number of grafted units within [ ], typically u may be in the range of 1 to 2000, or 1 to 500, or 1 to 250, or 1 to 50, 1 to 20, 1 to 10, or 1 to 4.

**[0189]** A more detailed description of the amine-functionalized carboxylic functionalized polymer is described in International Application PCT/US2008/082944 (based on U.S. Provisional Application 60/987,499), in particular see [0013] to [0021], [0027] to [0091] and the preparative examples 1 to 25 disclosed in paragraphs [0111] to [0112]. The disclosure provides an in-depth discussion on possible structures and methods of preparation of the amine-functionalized carboxylic functionalized polymer.

**[0190]** Typically the amine-functionalized additive may be based upon a polyisobutylene defined by BB in formula (4) or formula (5) above.

**[0191]** In one embodiment the non-borated dispersant comprises an amine having at least 3 or 4 aromatic groups may be represented by Formula (1) reacted with polyisobutylene anhydride.

**[0192]** When present, the non-borated dispersant may be present at 0.25 wt % to 8 wt %, or 0.5 wt % to 5 wt %, 1 wt % to 4.5 wt % or 1.6 wt % to 2.5 wt % of the lubricating composition.

#### Dispersant Viscosity Modifier

**[0193]** The lubricating composition of the disclosed technology in one embodiment further contains a dispersant viscosity modifier. When present the dispersant viscosity modifier may be present at 0.01 wt % to 3 wt %, or 0.05 wt % to 1.5 wt %, or 0.1 wt % to 1 wt %, or 0.1 to 0.5 wt %. In one embodiment the lubricating composition disclosed herein further comprises a dispersant viscosity modifier.

**[0194]** The dispersant viscosity modifier may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalized with an amine, or styrene-maleic anhydride copolymers reacted with an amine. More detailed description of dispersant viscosity modifiers are disclosed in International Publication WO2006/015130 or U.S. Pat. Nos. 4,863,623; 6,107,257; 6,107,258; 6,117,825; and 7,790,661. In one embodiment the dispersant viscosity modifier may include those described in U.S. Pat. No. 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described paragraphs [0065] to [0073]).

**[0195]** In one particular embodiment the dispersant viscosity modifier comprises an olefin copolymer further functionalized with a dispersant amine group. Typically, the olefin copolymer may be an ethylene-propylene copolymer.

**[0196]** The olefin copolymer has a number average molecular weight of 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

**[0197]** The dispersant amine group may be prepared/derived from reacting the olefin copolymer (typically, an ethylene-propylene copolymer) with an acylating agent (typically maleic anhydride) and an aromatic amine having a primary or secondary amino group. Typically, the dispersant viscosity modifier may be an ethylene-propylene copolymer acylated with maleic anhydride and reacted with an aromatic amine.

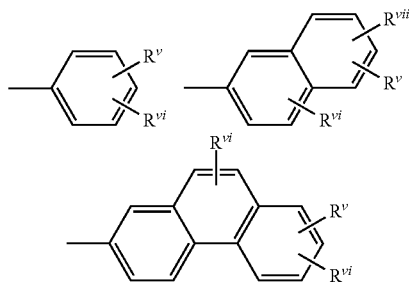
**[0198]** The formation of a dispersant viscosity modifier is well known in the art. The dispersant viscosity modifier may include for instance those described in U.S. Pat. No. 7,790,661 column 2, line 48 to column 10, line 38.

**[0199]** In one embodiment the dispersant viscosity modifier may be prepared by grafting of an olefinic carboxylic acid acylating agent onto a polymer of 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of C<sub>3-10</sub>  $\alpha$ -monoolefin, and from 0 to 15 mole percent of non-conjugated diene or triene, said polymer having an average molecular weight ranging from 5000 to 500,000, and further reacting said grafted polymer with an amine (typically an aromatic amine).

**[0200]** In another embodiment the dispersant viscosity modifier may be a reaction product of: (a) a polymer comprising carboxylic acid functionality or a reactive equivalent thereof, said polymer having a number average molecular weight of greater than 5,000; and (b) an amine component comprising at least one aromatic amine containing at least one amino group capable of condensing with said carboxylic acid functionality to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom, wherein said aromatic amine may be chosen from (i) a nitro-substituted aniline, (ii) an amine comprising two aromatic moieties linked by a —C(O)NR— group, a —C(O)O— group, an —O— group, an —N=N— group, or an —SO<sub>2</sub>— group where R may be hydrogen or hydrocarbyl, one of said aromatic moieties bearing said condensable amino group, (iii) an aminoquinoline, (iv) an aminobenzimidazole, (v) an N,N-dialkylphenylenediamine, (vi), an aminodiphenylamine (also N,N-phenyldiamine), and (vii) a ring-substituted benzylamine.

**[0201]** The aromatic amine of the dispersant viscosity modifier may also include those which can be represented by

the general structure  $\text{NH}_2\text{—Ar}$  or  $\text{T-NH—Ar}$ , where T may be alkyl or aromatic, Ar may be an aromatic group, including nitrogen-containing or amino-substituted aromatic groups and Ar groups including any of the following structures

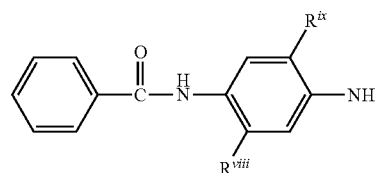


as well as multiple non-condensed or linked aromatic rings. In these and related structures,  $\text{R}^v$ ,  $\text{R}^{vi}$ , and  $\text{R}^{vii}$  can be independently, among other groups disclosed herein,  $\text{—H}$ ,  $\text{—C}_{1-18}$  alkyl groups, nitro groups,  $\text{—NH—Ar}$ ,  $\text{—N=N—Ar}$ ,  $\text{—NH—CO—Ar}$ ,  $\text{—OOC—Ar}$ ,  $\text{—OOC—C}_{1-18}$  alkyl,  $\text{—COO—C}_{1-18}$  alkyl,  $\text{—OH}$ ,  $\text{—O—(CH}_2\text{CH}_2\text{—O)}_n\text{C}_{1-18}$  alkyl groups, and  $\text{—O—(CH}_2\text{CH}_2\text{O)}_n\text{Ar}$  (where n may be 0 to 10).

**[0202]** Aromatic amines include those amines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The amines may be monoamines or polyamines. The aromatic ring will typically be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthalene. Examples of aromatic amines include aniline, N-alkylanilines such as N-methylaniline and N-butylaniline, di-(para-methylphenyl)amine, 4-aminodiphenylamine, N,N-dimethylphenylenediamine, naphthylamine, 4-(4-nitrophenylazo)aniline (disperse orange 3), sulphamethazine, 4-phenoxyaniline, 3-nitro-aniline, 4-aminoacetanilide (N-(4-aminophenyl)acetamide), 4-amino-2-hydroxy-benzoic acid phenyl ester (phenyl amino salicylate), N-(4-amino-phenyl)-benzamide, various benzylamines such as 2,5-dimethoxybenzylamine, 4-phenylazobenzylamine, and substituted versions of these. Other examples include para-ethoxyaniline, para-dodecylaniline, cyclohexyl-substituted naphthylamine, and thienyl-substituted aniline. Examples of other suitable aromatic amines include amino-substituted aromatic compounds and amines in which the amine nitrogen is a part of an aromatic ring, such as 3-aminoquinoline, 5-aminoquinoline, and 8-aminoquinoline. Also included are aromatic amines such as 2-aminobenzimidazole, which contains one secondary amino group attached directly to the aromatic ring and a primary amino group attached to the imidazole ring. Other amines include N-(4-anilinophenyl)-3-aminobutanamide or 3-amino propyl imidazole. Yet other amines include 2,5-dimethoxybenzylamine.

**[0203]** Additional aromatic amines and related compounds are disclosed in U.S. Pat. Nos. 6,107,257 and 6,107,258; some of these include aminocarbazoles, benzoimidazoles, aminoindoles, aminopyrroles, amino-indazolones, aminoperimidines, mercaptotriazoles, aminophenothiazines, aminopyridines, aminopyrazines, aminopyrimidines, pyridines, pyrazines, pyrimidines, ami-

nothiadiazoles, aminothiadiadiazoles, and aminobenzotriazoles. Other suitable amines include 3-amino-N-(4-anilinophenyl)-N-isopropyl butanamide, and N-(4-anilinophenyl)-3-((3-aminopropyl)-(cocoalkyl)amino) butanamide. Other aromatic amines which can be used include various aromatic amine dye intermediates containing multiple aromatic rings linked by, for example, amide structures. Examples include materials of the general structure:

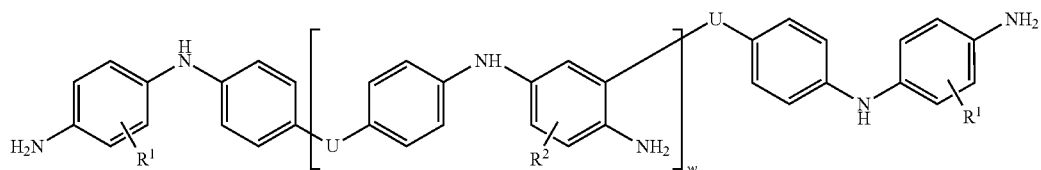


and isomeric variations thereof, where  $\text{R}^{viii}$  and  $\text{R}^{ix}$  are independently alkyl or alkoxy groups such as methyl, methoxy, or ethoxy. In one instance,  $\text{R}^{viii}$  and  $\text{R}^{ix}$  are both  $\text{—OCH}_3$  and the material is known as Fast Blue RR [CAS#6268-05-9].

**[0204]** In another instance,  $\text{R}^{ix}$  may be  $\text{—OCH}_3$  and  $\text{R}^{viii}$  may be  $\text{—CH}_3$ , and the material is known as Fast Violet B [99-21-8]. When both  $\text{R}^{viii}$  and  $\text{R}^{ix}$  are ethoxy, the material is Fast Blue BB [120-00-3]. U.S. Pat. No. 5,744,429 discloses other aromatic amine compounds, particularly aminoalkylphenothiazines. N-aromatic substituted acid amide compounds, such as those disclosed in U.S. Patent Application 2003/0030033 A1, may also be used for the purposes of the disclosed technology. Suitable aromatic amines include those in which the amine nitrogen is a substituent on an aromatic carboxylic compound, that is, the nitrogen is not  $\text{sp}^2$  hybridized within an aromatic ring.

**[0205]** The aromatic amine may also comprise an amine formed by reacting an aldehyde with 4-aminodiphenylamine. The resultant amine may be described as an alkylene coupled amine having at least 4 aromatic groups, at least one  $\text{—NH}_2$  functional group, and at least 2 secondary or tertiary amino groups. The aldehyde may be aliphatic, alicyclic or aromatic. The aliphatic aldehyde may be linear or branched. Examples of a suitable aromatic aldehyde include benzaldehyde or o-vanillin. Examples of an aliphatic aldehyde include formaldehyde (or a reactive equivalent thereof such as formalin or paraformaldehyde), ethanal or propanal. Typically the aldehyde may be formaldehyde or benzaldehyde. Alternatively, this aromatic amine may also be prepared by the methodology described in Berichte der Deutschen Chemischen Gesellschaft (1910), 43, 728-39.

**[0206]** The aromatic amine formed by coupling an aldehyde and 4-aminodiphenylamine is described European Patent application EP 2 401 348 A in and may also be represented by the formula:



wherein each variable

$R^1$  may be hydrogen or a  $C_{1-5}$  alkyl group (typically hydrogen);

$R^2$  may be hydrogen or a  $C_{1-5}$  alkyl group (typically hydrogen);

U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U may be aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and

w may be 0 to 9 or 0 to 3 or 0 to 1 (typically 0).

**[0207]** In one embodiment the aromatic amine includes 4-aminodiphenylamine, aldehyde (typically formaldehyde) coupled 4-aminodiphenylamine, nitro-aniline (3-nitro-aniline), disperse orange-3 (D03), or mixtures thereof.

**[0208]** A lubricating composition may be prepared by adding the product of the process described herein to an oil of lubricating viscosity, optionally in the presence of other performance additives (as described herein below).

#### Other Performance Additives

**[0209]** The lubricating composition of the disclosed technology optionally comprises other performance additives. The other performance additives include at least one of metal deactivators, viscosity modifiers, friction modifiers, antiwear agents, corrosion inhibitors, extreme pressure agents, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

**[0210]** In one embodiment the friction modifier may be chosen from long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimidides; fatty alkyl tartramides; fatty glycolates; and fatty glycolamides. The friction modifier may be present at 0 wt % to 6 wt %, or 0.01 wt % to 4 wt %, or 0.05 wt % to 2 wt %, or 0.1 wt % to 2 wt % of the lubricating composition.

**[0211]** As used herein the term “fatty alkyl” or “fatty” in relation to friction modifiers means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain.

**[0212]** Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimidides; fatty alkyl tartramides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxyated fatty amines; borated alkoxyated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxyated alcohols; condensation prod-

ucts of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

**[0213]** Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

**[0214]** In another embodiment the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride.

**[0215]** The lubricating composition optionally further includes at least one antiwear agent.

**[0216]** Examples of suitable antiwear agents include titanium compounds, tartrates, tartrimidides, oil soluble amine salts of phosphorus compounds, sulfurized olefins, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thio-carbamates, and bis(S-alkyldithiocarbamyl) disulfides. The antiwear agent may in one embodiment include a tartrate, or tartramide as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125. The tartrate or tartramide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups may be at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in US Patent Application 20050198894.

**[0217]** Another class of additives includes oil-soluble titanium compounds as disclosed in U.S. Pat. No. 7,727,943 and US2006/0014651. The oil-soluble titanium compounds may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In one embodiment the oil soluble titanium compound may be a titanium (IV) alkoxide. The titanium alkoxide may be formed from a monohydric alcohol, a polyol or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms. In one embodiment, the titanium alkoxide may be titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide may be titanium (IV) 2-ethylhexoxide. In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. In one embodiment, the 1,2-vicinal diol comprises a fatty acid mono-ester of glycerol, often the fatty acid may be oleic acid.

**[0218]** In one embodiment, the oil soluble titanium compound may be a titanium carboxylate. In a further embodiment the titanium (IV) carboxylate may be titanium neodecanoate.

**[0219]** The lubricating composition may in one embodiment further include a phosphorus-containing antiwear

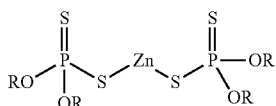


agent. Typically the phosphorus-containing antiwear agent may be a zinc dialkyldithiophosphate, phosphite, phosphate, phosphonate, and ammonium phosphate salts, or mixtures thereof. Zinc dialkyldithiophosphates are known in the art. The antiwear agent may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 0.9 wt % of the lubricating composition.

**[0220]** In one embodiment the lubricating composition may further include a phosphorus-containing antiwear agent based upon zinc dialkyldithiophosphate, or mixtures thereof.

**[0221]** When present the amount of zinc dialkyldithiophosphate present may deliver 100 ppm to 1000 ppm, or 200 ppm to 900 ppm, or 350 ppm to 900 ppm of phosphorus.

**[0222]** The zinc dialkyldithiophosphate may be derived from aliphatic or aromatic hydrocarbyl alcohols; the hydrocarbyl; alcohols may be primary or secondary alcohols. A zinc dialkyldithiophosphate (or ZDDP) derived from secondary alcohols is said to be a secondary ZDDP. A ZDDP derived from primary alcohols is said to be a primary ZDDP. ZDDP prepared from a mixture of primary and secondary alcohols is said to be a mixed primary/secondary ZDDP. In one embodiment the ZDDP may be represented by the following structure:



wherein each R may be independently a primary or secondary hydrocarbyl group containing from 1 to 24, for example from 2 to 12, carbon atoms and including groups such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic hydrocarbyl groups. In an embodiment, R may be alkyl groups of 2 to 8 carbon atoms. R may be, for example, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylehexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, and butenyl.

**[0223]** The R group of the zinc dithiophosphate may be derived, for example, from a primary alcohol such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, dodecanol, octadecanol, propenol, butenol, 2-ethylhexanol; a secondary alcohol such as isopropyl alcohol, secondary butyl alcohol, isobutanol, 3-methylbutan-2-ol, 2-pentanol, 4-methyl-2-pentanol, 2-hexanol, 3-hexanol, amyl alcohol, an aryl alcohol such as phenol, substituted phenol (particularly alkylphenol such as butylphenol, octylphenol, nonylphenol, dodecylphenol), disubstituted phenol. Certain primary diols may also be used to prepare ZDDP; suitable primary diols include ethylene glycol, propylene glycol, and esters of polyhydric alcohol such as glycerol monooleate and combinations thereof. ZDDP may be prepared from a combination of primary alcohols and primary diols.

**[0224]** In one embodiment the R group of the ZDDP may be independently a primary alkyl, a secondary alkyl, an aryl group, or mixtures thereof.

**[0225]** In one embodiment the R group of the ZDDP may be a secondary alkyl group.

**[0226]** Extreme Pressure (EP) agents include compounds that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, dimercapthiadiazole or CS<sub>2</sub> deriva-

tives of dispersants (typically succinimide dispersants), derivative of chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulfurized olefins (such as sulfurized isobutylene), a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, organic sulfides and polysulfides such as dibenzyldisulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphorus sulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyl-dithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P205; and mixtures thereof (as described in U.S. Pat. No. 3,197,405).

**[0227]** Foam inhibitors that may be useful in the compositions of the disclosed technology include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

**[0228]** Pour point depressants that may be useful in the compositions of the disclosed technology include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

**[0229]** Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

**[0230]** Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

**[0231]** Seal swell agents include sulpholene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

#### INDUSTRIAL APPLICATION

**[0232]** The internal combustion engine may be a 4-stroke engine. The internal combustion engine may or may not have an Exhaust Gas Recirculation system. The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), or systems employing selective catalytic reduction (SCR).

**[0233]** The lubricating composition may be characterized as having (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulfated ash content of 0.5 wt % to 1.5 wt % or less.

**[0234]** The lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.2 wt % to 0.4 wt % or less, (ii) a phosphorus content of 0.08 wt % to 0.15 wt %, and (iii) a sulfated ash content of 0.5 wt % to 1.5 wt % or less.

**[0235]** The lubricating composition may be characterized as having a sulfated ash content of 0.5 wt % to 1.2 wt %.

**[0236]** The lubricating composition may have a total sulfated ash content of 1.2 wt % or less.

**[0237]** The sulfur content of the lubricating composition may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment the sulfur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %. The phosphorus content may be 0.2 wt % or less, or 0.12 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or 0.08 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment the phosphorus content may be 0.04 wt % to 0.12 wt %. In one embodiment the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content may be 0.3 wt % to 1.2 wt %, or 0.5 wt % to 1.1 wt % of the lubricating composition. In one embodiment the sulfated ash content may be 0.5 wt % to 1.1 wt % of the lubricating composition.

**[0238]** In one embodiment the lubricating composition may be characterized as having (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.15 wt % or less, and (iii) a sulfated ash content of 0.5 wt % to 1.5 wt % or less.

**[0239]** The lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.2 wt % to 0.4 wt % or less, (ii) a phosphorus content of 0.08 wt % to 0.15 wt %, and (iii) a sulfated ash content of 0.5 wt % to 1.5 wt % or less.

**[0240]** The lubricating composition may be characterized as having a sulfated ash content of 0.5 wt % to 1.2 wt %.

**[0241]** The lubricating composition may have a SAE viscosity grade of XW—Y, wherein X may be 0, 5, 10, or 15; and Y may be 16, 20, 30, or 40.

**[0242]** The internal combustion engine disclosed herein may have a steel surface on a cylinder bore, cylinder block, or piston ring.

**[0243]** The internal combustion engine may have a surface of steel, or an aluminium alloy, or an aluminium composite.

**[0244]** Typically the compression-ignition internal combustion engine has a maximum laden mass over 3,500 kg.

**[0245]** The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

#### EXAMPLES

**[0246]** A series of 15W-40 engine lubricants in Group II base oil of lubricating viscosity are prepared containing the additives described above as well as conventional additives including polymeric viscosity modifier, ashless succinimide dispersant, overbased detergents, as well as other performance additives as follows (Table 1). The phosphorus, sulfur and ash contents of each of the examples are also presented in the table in part to show that each example has a similar amount of these materials and so provide a proper comparison between the comparative and invention examples.

TABLE

Lubricating Compositions <sup>1</sup>						
	EX1	EX2	EX3	EX4	EX5	EX6
	15W-40					
Base Oil	Balance to 100% <sup>1</sup>					
Overbased calcium sulfonate (Metal ratio 9.2) <sup>2</sup>	0.70	0.70	1.04	1.04	1.04	1.04
Calcium sulfonate (metal ratio 2.7) <sup>3</sup>	0.265	0.265	0.80	0.80	0.80	0.80
Overbased Calcium phenate <sup>4</sup>	0.49	0.49	0	0	0	0
“Neutral” Calcium phenate	0.29	0.29	0	0	0	0
Succinimide dispersant <sup>5</sup>	3.5	3.5	1.75	0	1.75	1.75
Aryl amine succinimide dispersant <sup>6</sup>	0.5	0.3	0.5	0.3	0.3	0.5
Borated dispersant A <sup>7</sup>	0	0	0	0	0.54	0
Borated Dispersant B <sup>8</sup>	0	0	0	1.5	0	0
Borate ester (2-propylheptyl)	0	0	0	0	0	0.5
Secondary ZDDP (C3-6)	0.72	0.72	0.72	0.72	0.72	0.72
Hindered phenol ester antioxidant	0.2	0.2	0.2	0.2	0.2	0.2
Other Antioxidants	0.2	0.2	0.2	0.2	0.2	0.2
Other Additives <sup>9</sup>	0.02	0.02	0.02	0.02	0.02	0.02
OCP Viscosity Index	0.7	0.7	0.7	0.8	0.7	0.7
Improver						
Calcium (weight %)	0.262	0.262	0.288	0.287	0.287	0.288
Phosphorus (weight %)	0.0803	0.0803	0.0803	0.0803	0.0803	0.0803
Boron (ppm)	0	0	0	0.0134	0.0152	0.0112
Detergent Substrate	1.1	1.1	1.1	1.1	1.1	1.1
Sulfated Ash	1.2	1.2	1.2	1.2	1.2	1.2
TBN	8	8	8	7.5	8	8

<sup>1</sup>All amounts shown above are in weight percent and are on an oil-free basis unless otherwise noted.

<sup>2</sup>Overbased alkylbenzene sulfonate with TBN 520 mg KOH/g

<sup>3</sup>Low overbased alkylbenzene sulfonate with TBN 160 mg KOH/g

<sup>4</sup>Overbased calcium sulfurized phenate with TBN 420 mg KOH/g

<sup>5</sup>Conventional polyisobutenyl succinimide dispersant, aminated with polyethylene polyamines (PIB Mn ~2200; TBN 54 mg KOH/g)

<sup>6</sup>Conventional polyisobutenyl succinimide dispersant, aminated with polyaromatic polyamine (PIB Mn ~2200; TBN ~6 mg KOH/g)

<sup>7</sup>Borated polyisobutenyl succinimide dispersant (PIB Mn 1200; TBN 90 mg KOH/g; 2.85 wt %B)

<sup>8</sup>Borated polyisobutenyl succinimide dispersant (PIB Mn ~2200; TBN 54 mg KOH/g; 0.6 wt % B)

<sup>9</sup>Other additives include low levels of corrosion inhibitors, foam inhibitor, and pourpoint depressant

[0247] The lubricants are evaluated for deposit control, copper and lead corrosion, and friction and wear in a series of bench tests and fired engine tests. Deposit control is evaluated using industry standard tests TEOST 33C (ASTM D6335), MHT TEOST (ASTM D7097B), the Caterpillar 1K (ASTM D6750) single cylinder engine test, and the Mack T-12 engine test. Corrosion is evaluated using an extended version of the high temperature corrosion bench test (HTCBT as described in ASTM D6594. This test is run for

168 hours, the table below shows the results after the double length HTCBT test), which is carried out according to the procedure of ASTM D6594 extended to 336 hours, OM501LA-CEC L-101-08, OM646LA-CEC L-099-08, as well as the Mack T-12 (ASTM D7422) engine test. Wear and friction are evaluated using a reciprocating rig bench test and the GM 6.5 L roller follower wear test (RFWT, ASTM D5966). Engine tests may include those run under the test procedures above, and typical test parameters for the each test are presented in the table below.

TABLE 2

Bench Test Results						
	EX1*	EX2*	EX3*	EX4	EX5	EX6
<u>TEOST 33C</u>						
Total Deposits (mg)	13.8	6.9	4.0	2.8	3.7	3.6
<u>MHT TEOST</u>						
Total Deposits (mg)	77.2	73	59.5	57.6	54.2	51.6
<u>Corrosion Bench Test</u>						
Copper @ 240 hr (ppm)	8	9	14	3	5	4
Copper @ 336 hr (ppm)	247	268	153	266	172	5
Lead @ 240 hr (ppm)	30	72	17	1	3	2
Lead @ 336 hr (ppm)	34	74	17	1	3	2
<u>Reciprocating Rig</u>						
Wear Scar (microns)	345	346	326			317
Coefficient of friction	0.124	0.125	0.121			0.121
<u>Mack T-12</u>						
Total merits					1598	1712.9
Ave. Liner Wear (□m)					19	13.3
Ave. Top Ring Weight Loss (mg)					44	84
EOT Lead (ppm)					21	8
D Lead 250-300 hr (ppm)					10	3
<u>GM 6.5 L RFWT</u>						
Pin Wear (mils)					0.12	0.28
<u>Caterpillar 1K</u>						
Weighted demerits					304	263
Top Groove Fill (%)					6	7
Top Land Heavy Carbon (%)					1	0

\*Comparative Examples

	Industry limits for targeted category	Industry limits for higher performance categories	EX5	EX6
<u>Mack T-12</u>				
Total merits	—	1,000 min	1598	1712.9
Ave. Liner Wear (□m)	30 max	26 max	19	13.3
Ave. Top Ring Weight Loss (mg)	120 max	117 max	44	84
EOT Lead (ppm)	65 max	42 max	21	8
D Lead 250-300 hr (ppm)	—	18 max	10	3
Oil consumption (phase II) (g/h)	—	95 max	50.3	46.9
<u>GM 6.5 L RFWT</u>				
Pin Wear (mils)	CH-4 0.45 max	CI-4 0.3 max	0.12	0.28
<u>Caterpillar 1K</u>				
Weighted demerits	332 max		304	263
Top Groove Fill (%)	24 max		6	7
Top Land Heavy Carbon (%)	4 max		1	0
<u>Daimler OM501LA</u>				
Piston cleanliness (merit)	MB 228.1 16.0 min	MB 228.3 19.0 min	23	
Bore polish (%)	3.0 max	3.0 max	0	

TABLE 2-continued

Bench Test Results			
Average engine sludge (merit)	9.0 min	9.0 min	9.3
Oil consumption (g/h)	50.0 max	30.0 max	24.4
Ring sticking (ASF)	1.0 max	1.0 max	0
General engine deposits (demerits)	3.0 max	2.0 max	1.5
Wear rating (demerits)	3.0 max	3.0 max	1.8
Average cylinder wear (mm)	0.008 max	0.008 max	0.0005
Turbocharger deposits (demerit)	3.0 max	2.0 max	1
Daimler OM646LA	MB 228.1	MB 228.3	
Cam wear, inlet ( $\mu\text{m}$ )	120 max	100 max	30.3
Cam wear, outlet ( $\mu\text{m}$ )	155 max	130 max	53.8
Cylinder wear ( $\mu\text{m}$ )	5.0 max	5.0 max	1.1
Max bore polishing (%)	4.0 max	3.5 max	1.7
Piston cleanliness (merit)	10.0 min	12.0 min	18.04
Average engine sludge	8.6 min	8.8 min	9.1
Viscosity increase at 100° C. (%)	100 max	100 max	66.9
Ring stick	0	0	0
Bearing wear main/con rod ( $\mu\text{m}$ )	2.1/2.1 max	2.1/2.1 max	0.3/0.6
Piston ring wear axial ( $\mu\text{m}$ )	10.4/6.0/5.0 max	10.4/6.0/5.0 max	1.4/0.4/0.2
Piston ring wear radial ( $\mu\text{m}$ )	10.4/12.0/8.0 max	10.4/12.0/8.0 max	4.0/6.8/2.7
Timing chain wear (%)	0.4 max	0.4 max	0.15
Oil consumption (g/test)	7000 max	7000 max	5021
Soot (%)	3.0-6.0	3.0-6.0	5.8

**[0248]** The results obtained indicate that the lubricating composition may have at least one of deposit control, wear control and/or Cu/Pb corrosion control.

**[0249]** 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. The products formed thereby, including the products formed upon employing lubricant composition of the disclosed technology in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the disclosed technology; the disclosed technology encompasses lubricant composition prepared by admixing the components described above.

**[0250]** 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 may be used together with ranges or amounts for any of the other elements.

**[0251]** As used herein, the term “hydrocarbyl substituent” or “hydrocarbyl group” is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to

the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; 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; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term “hydrocarbyl substituent” or “hydrocarbyl group” is described in paragraphs [0118] to [0119] of International Publication WO2008147704, or a similar definition in paragraphs [0137] to [0141] of published application US 2010-0197536.

**[0252]** As described hereinafter the number average molecular weight of the dispersant viscosity modifier and viscosity modifier has been determined using known methods, such as GPC analysis using polystyrene standards. Methods for determining molecular weights of polymers are well known. The methods are described for instance: (i) P. J. Flory, “Principles of Polymer Chemistry”, Cornell University Press 91953), Chapter VII, pp 266-315; or (ii) “Macromolecules, an Introduction to Polymer Science”, F. A. Bovey and F. H. Winslow, Editors, Academic Press (1979), pp 296-312.

**[0253]** While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A method of lubricating a compression-ignition internal combustion engine with a maximum laden mass over 2,700 kg comprising supplying to the engine a lubricating composition comprising:

an oil of lubricating viscosity,

a 300 TBN or higher alkaline earth metal sulfonate detergent having a metal ratio of 9.2 to 40,

an alkaline earth metal sulfonate detergent having a metal ratio of 2.7 to 5, and a TBN of 81 to 180 mg KOH/g (as measured by ASTM D2896-11),

wherein the sulfonate detergents provide a total amount of sulfonate substrate of 1.0 wt % to 3 wt % of the lubricating composition,

0.1 to 1.2 wt % of antioxidant, wherein at least 20 wt % of the antioxidant is a phenolic antioxidant,

a borated compound present in an amount to deliver 75 to 152 ppm of boron and the borated compound is chosen from:

a borate-ester having the formula:



where each R is independently an alkyl group having 10 to 32 carbon atoms, and

a borated polyisobutenyl succinimide dispersant derived from a PIB having an Mn of from 1,200 to 2,200, and

wherein

the lubricating composition has a sulfated ash content of 0.4 wt % to 1.2 wt % and

the lubricating composition has a TBN of 7.5 to 15 mg KOH/g (as measured by ASTM D2896-11).

2. The method of claim 1, wherein the lubricating composition is characterized as having (i) a sulfur content of 0.5 wt % or less, and (ii) a phosphorus content of 0.15 wt % or less.

3. The method of claim 1, wherein the oil of lubricating viscosity comprises a base oil selected from one or more of an API Group I, II, III, IV, V, or mixtures thereof.

4. The method of claim 1, wherein the antioxidant comprises an aminic antioxidant.

5. The method of claim 4, wherein the antioxidant comprises at most 60 wt % of the aminic antioxidant.

6. The method of claim 1, wherein the antioxidant comprises a sulfurized olefin antioxidant.

7. The method of claim 6, wherein the antioxidant comprises at most 60 wt % of the sulfurized olefin antioxidant.

8. The method of claim 1, wherein the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof, and wherein the antioxidant is present at 0.1 wt % to 3 wt %.

9. The method of claim 1, wherein the lubricating composition has a total base number (TBN) content of 7.5 to 10 mg KOH/g.

10. The method of claim 1, wherein the sulfonate detergents deliver 1.05 to 1.2 wt % of substrate to the lubricating composition.

11. The method of claim 1, wherein the lubricating composition comprises 0 wt % to 0.2 wt % of a phenolic based detergent.

12. The method of claim 11, wherein the lubricating composition comprises 0 wt % of a phenolic based detergent.

13. The method of claim 1, wherein the lubricating composition further comprises a dispersant viscosity modifier.

14. The method of claim 13, wherein the dispersant viscosity modifier is an olefin copolymer further functionalized with a dispersant amine group.

15. The method of claim 13, wherein the dispersant viscosity modifier is prepared by:

grafting an olefinic carboxylic acid acylating agent onto a polymer of 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of C<sub>3-10</sub> alpha monoolefin, and from 0 to 15 mole percent of non-conjugated diene or triene, said polymer having number average molecular weight ranging from 5000 to 500,000; and

reacting the resultant grafted polymer with an amine.

16. The method of claim 1, wherein the lubricating composition further comprises a non-borated dispersant.

17. The method of claim 16, wherein the non-borated dispersant is an amine-functionalized additive derived from an amine having at least 4 aromatic groups, at least one —NH<sub>2</sub> functional group, and at least 2 secondary or tertiary amino groups.

18. The method of claim 1, wherein the lubricating composition further comprises a zinc dialkyldithiophosphate.

19. The method of claim 18, wherein the zinc dialkyldithiophosphate is a primary zinc dialkyldithiophosphate, or a secondary zinc dialkyldithiophosphate.

20. The method of claim 18, wherein the zinc dialkyldithiophosphate is present to deliver 100 ppm to 1000 ppm of phosphorus.

21. The method of claim 1, wherein the internal combustion engine has a steel surface on a cylinder bore, cylinder block, or piston ring.

22. The method of claim 1, wherein the internal combustion engine has a surface of steel, or an aluminum alloy, or an aluminum composite.

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