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(54) **Titre : PROCEDE DE LUBRIFICATION D'UN MOTEUR A COMBUSTION INTERNE**
(54) **Title: METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE**

(57) **Abrégé/Abstract:**

The invention 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 sulphonate 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 sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and wherein the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

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(54) Title: METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE

(57) Abstract: The invention 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 sulphonate 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 sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and wherein the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

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TITLE

METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE

FIELD OF INVENTION

[0001] The invention 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 sulphonate 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, the total amount of soap delivered by the alkaline earth metal sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

BACKGROUND OF THE INVENTION

[0002] 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. Patent 2,680,96, Walker et al., June 1 , 1954; see also U.S. Patent 3,372, 1 16, Meinhardt, March 6, 1968.

[0003] 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 C 12 alkyl phenols may contain residual monomeric C12 alkyl phenol species.

[0004] US Patent 7,943,796 (Campbell et al, 4 February 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 ^{o}C and a final boiling point of no more than about 325 ^{o}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.

[0005] US Patent 7,435,709 (Stonebaker et al, 1 March 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.

[0006] US Patent 8,183,192 (Sinquinn et al, 4 August 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 ^{o}C and a final boiling point of greater than 325 ^{o}C and up to about 400 ^{o}C as measured by ASTM D86. Also disclosed is a propylene oligomer having an initial boiling point of at least about 195 ^{o}C and a final boiling point of greater than 325 ^{o}C and up to about 400 ^{o}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

[0007] US Patent 8,207,380 (Campbell et al., 30 October 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 a acid catalyst. The alkylated hydroxyaromatic compound has been determined to be substantially free of endocrine disruptive chemicals when the effects were quantified on pubertal development and thyroid function in the intact juvenile female rat.

[0008] US Patent 8,198,225 (Harrison et al., 4 June 2009) discloses an 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

[0009] 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 hydroxyaromatic 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

[0010] International publication WO 2013/059173A1 (Cook et al, 25 April 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.

[0011] There is interest, therefore, in developing 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.

SUMMARY OF THE INVENTION

[0012] The present invention 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.

[0013] 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.

[0014] 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.

[0015] 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 invention is intended to encompass a method of lubricating a compression ignited internal combustion engine, as well as spark assisted compression ignited internal combustion engines.

[0016] 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 sulphonate detergents described herein, the soap or substrate is a neutral salt of an alkylbenzenesulphonic acid.

[0017] As used herein all total base number values cited are determined by ASTM Method D2896-11.

[0018] The invention 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:

an oil of lubricating viscosity,

a 300 TBN or higher alkaline earth metal sulphonate 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,

the ratio of higher alkaline earth metal sulphonate detergent to lower alkaline earth metal sulphonate detergent is 80:20 to 20:80,

the total amount of soap delivered by the alkaline earth metal sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and

the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

[0019] In one embodiment the invention 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:

an oil of lubricating viscosity,

a 300 TBN or higher alkaline earth metal sulphonate detergent having a metal ratio of 10 to 40,

a 80 TBN or lower alkaline earth metal sulphonate detergent having a metal ratio of 1 to 5,

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,

the ratio of higher alkaline earth metal sulphonate detergent to lower alkaline earth metal sulphonate detergent is 80:20 to 20:80,

the total amount of soap delivered by the alkaline earth metal sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and

the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

[0020] In one embodiment the invention 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:

an oil of lubricating viscosity,

a 300 TBN or higher alkaline earth metal sulphonate detergent having a metal ratio of 10 to 40,

a 80 TBN or lower alkaline earth metal sulphonate detergent having a metal ratio of 1 to 5,

a magnesium sulphonate 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,

the ratio of higher alkaline earth metal sulphonate detergent to lower alkaline earth metal sulphonate detergent is 80:20 to 20:80,

the total amount of soap delivered by the alkaline earth metal sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and

the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

[0021] In one embodiment the lubricating composition comprises 0 wt % to 0.1 wt % of a phenolic based detergent.

[0022] In a further embodiment the lubricating composition comprises 0 wt % of a phenolic based detergent.

[0023] The phenolic based detergent may be a phenate.

[0024] The phenolic based detergent may be chosen from a phenate, and a salycilate.

[0025] The phenolic based detergent may be chosen from a phenate, a salycilate, and a salixarate.

[0026] The phenate may be a non-sulphur containing phenate, sulphur containing phenate, or a “hybrid” detergent formed with mixed surfactant system, wherein the hybrid is a mixed phenate-salicylate, a sulphonate-phenate, or a sulphonate-phenate-salicylate.

[0027] In one embodiment the lubricating composition comprises 0 wt % of the phenolic based detergent. In this embodiment the lubricating composition comprises only sulphonate detergents.

[0028] 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.

[0029] 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 3,00 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 is set by national government and may be 10,000 kg, or 9,000 kg, or 8,000 kg, or 7,500 kg.

[0030] 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.

[0031] 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 communing 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.

[0032] In one embodiment the internal combustion engine is a heavy duty diesel compression ignited (or spark assisted compression ignited) internal combustion engine.

[0033] In another embodiment the invention 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

[0034] The present invention provides a method for lubricating an internal combustion engine and a use as disclosed above.

Oils of Lubricating Viscosity

[0035] 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, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Application 2010/197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in US Patent Application 2010/197536, see [0075] to [0076]). Synthetic oils may also 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.

[0036] Oils of lubricating viscosity may also be defined as specified in April 2008 version of "Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories". The API Guidelines are also summarised in US Patent US 7,285,516 (see column 11, line 64 to column 12, line 10).

[0037] In one embodiment the oil of lubricating viscosity may be an API Group I to IV mineral oil, an ester or a synthetic oil, or mixtures thereof. In one embodiment the oil of lubricating viscosity may be an API Group II, Group III, Group IV mineral oil, an ester or a synthetic oil, or mixtures thereof.

[0038] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the additives of the invention and the other performance additives.

[0039] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention (comprising the additives disclosed herein) 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 these additives 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. Typically the lubricating composition of the invention comprises at least 50 wt %, or at least 60 wt %, or at least 70 wt %, or at least 80 wt % of an oil of lubricating viscosity.

<u>Sulphonate Detergent</u>

[0040] 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.

[0041] 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.

[0042] The lubricating composition disclosed herein comprises at least one calcium sulphonate detergent described herein.

[0043] In a different embodiment the lubricating composition comprises at least one or at least two other sulphonate detergents. The sulphonate detergents of the invention are known to a person skilled in the art.

[0044] In another embodiment the lubricating composition further comprises another sulphonate detergent, typically a magnesium, sodium or zinc overbased sulphonate. Typically any additional sulphonate detergent may be a magnesium or sodium sulphonate detergent, with magnesium sulphonate the more typical.

[0045] In one embodiment the lubricating composition comprises a 300 TBN or higher alkaline earth metal sulphonate detergent having a metal ratio of 10 to 40, and a 80 TBN or lower alkaline earth metal sulphonate detergent having a metal ratio of 1 to 5.

[0046] In one embodiment the lubricating composition comprises a300 TBN or higher alkaline earth metal sulphonate detergent comprises a magnesium sulphonate detergent having a metal ratio of 10 to 40, and a 80 TBN or lower alkaline earth metal sulphonate detergent comprising a calcium sulphonate detergent having a metal ratio of 1 to 5.

[0047] In one embodiment the lubricating composition comprises 300 TBN or higher alkaline earth metal sulphonate detergent comprising a mixture of a calcium sulphonate detergent having a metal ratio of 10 to 40, and a magnesium sulphonate detergent having a metal ratio of 10 to 40, and a 80 TBN or lower alkaline earth metal sulphonate detergent comprises a calcium sulphonate detergent having a metal ratio of 1 to 5.

[0048] The 300 TBN or higher alkaline earth metal sulphonate detergent and the 80 TBN or lower alkaline earth metal sulphonate detergent may be prepared from the same or different hydrocarbyl-substituted sulphonic acids. Typically the hydrocarbyl-substituted sulphonic acids are alkyl-substituted sulphonic acids.

[0049] The sulphonate may be prepared from a mono- or di- hydrocarbyl-substituted benzene (or naphthalene, indenyl, indanyl, or bicyclopentadienyl) sulphonic acid, wherein the hydrocarbyl group may contain 6 to 40, or 8 to 35 or 9 to 30 carbon atoms.

[0050] 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, nonodecyl, eicosyl, un-eicosyl, do-eicosyl, tri-eicosyl, tetra-eicosyl, penta-eicosyl, hexa-eicosyl or mixtures thereof.

[0051] In one embodiment the hydrocarbyl-substituted sulphonic acid may include polypropene benzenesulphonic acid and C_{16}-C_{24} alkyl benzenesulphonic acid, or mixtures thereof.

[0052] In one embodiment the 300 TBN sulphonate detergent may be a predominantly linear alkylbenzene sulphonate 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 US 7,407,919). The predominantly linear alkylbenzene sulphonate detergent may be particularly useful for assisting in improving fuel economy.

[0053] Typically the 300 TBN or higher alkaline earth metal sulphonate 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.

[0054] The calcium sulphonate detergent having a metal ratio of 10 to 40 may have a TBN of 350 to 500, or 375 to 425 mg KOH/g.

[0055] For example the calcium sulphonate may have a TBN ranging from 350 to 500 and a metal ratio of 20 to 30, or may have a TBN of 375 to 425 mg KOH/g; and a metal ratio of 22 to 25.

[0056] When neutral or slightly basic, a calcium sulphonate detergent may have TBN of 1 to 80, or 1 to 75, typically 2 to 50 mg KOH/g, or 5 to 35 mg KOH/g.

[0057] The calcium sulphonate detergent having a metal ratio of 1 to 5 may have a TBN of 1 to 80, or 2 to 40, or 5 to 35 mg KOH/g. Typically the calcium sulphonate detergent having a metal ratio of 1 to 5 has a TBN of 5 to 35 mg KOH/g.

[0058] In one embodiment the lubricating composition comprises a calcium sulphonate detergent having a metal ratio of 10 to 40, and a calcium sulphonate detergent having a metal ratio of 1 to 5.

[0059] In one embodiment the lubricating composition comprises a calcium sulphonate detergent having a metal ratio of 10 to 40, a calcium sulphonate detergent having a metal ratio of 1 to 5, and a magnesium sulphonate detergent having a metal ratio of 12 to 40.

[0060] The magnesium sulphonate 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 sulphonate may have the same or different hydrocarbyl-substituted sulphonic acids, and are defined the same as described above for calcium sulphonate detergents.

[0061] If present the other sulphonate (typically magnesium sulphonate) 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 sulphonate detergents, and optionally a magnesium sulphonate detergent which is present or absent in different embodiment.

[0062] In one embodiment at least two of the sulphonate detergents are calcium sulphonate detergents. For example, the 80 TBN or lower alkaline earth metal sulphonate detergent may be a calcium sulphonate, or the 300 TBN or higher alkaline earth metal sulphonate detergent may be a calcium or magnesium sulphonate.

[0063] In one embodiment the 300 TBN or higher alkaline earth metal sulphonate detergent comprises a calcium sulphonate detergent having a metal ratio of 10 to 40, and the 80 TBN or lower alkaline earth metal sulphonate detergent comprises a calcium sulphonate detergent having a metal ratio of 1 to 5.

[0064] In one embodiment the 300 TBN or higher alkaline earth metal sulphonate detergent comprises a magnesium sulphonate detergent having a metal ratio of 10 to 40, and the 80 TBN or lower alkaline earth metal sulphonate detergent comprises a calcium sulphonate detergent having a metal ratio of 1 to 5.

[0065] In one embodiment the 300 TBN or higher alkaline earth metal sulphonate detergent comprises a mixture of a calcium sulphonate detergent having a metal ratio of 10 to 40, and a magnesium sulphonate detergent having a metal ratio of 10 to 40, and the 80 TBN or lower alkaline earth metal sulphonate detergent comprises a calcium sulphonate detergent having a metal ratio of 1 to 5.

[0066] The 300 TBN or higher alkaline earth metal sulphonate detergent mixture comprise calcium sulphonate detergent having a metal ratio of 16 to 20, and the magnesium sulphonate detergent having a metal ratio of 12 to 40.

[0067] The 300 TBN or higher alkaline earth metal sulphonate detergent mixture comprise calcium sulphonate detergent having a metal ratio of 22 to 25, and the magnesium sulphonate detergent having a metal ratio of 14 to 25.

Dispersant

[0068] The lubricating composition comprises:

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 (a non-borated polyisobutylene succinimide), wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 350 to 5000, or 750 to 3000 or 1550 to 2500.

[0069] The succinimide dispersants of both the borated polyisobutylene succinimide and the polyisobutylene succinimide may be derived from an aliphatic polyamine, or mixtures thereof.

[0070] 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, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0071] The borated and non-borated polyisobutylene succinimide dispersants and their preparation are disclosed, for instance in US Patents 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.

[0072] The borated polyisobutylene succinimide may be prepared borated using a variety of agents including boric acid (for example, metaboric acid,

HBO_2, orthoboric acid, H_3BO_3, and tetraboric acid, $H_2B_4O_7$), boric oxide, or boron trioxide.

[0073] The borated dispersant may be prepared by blending the boron compound and the N-substituted long chain alkenyl succinimides and heating them at a suitable temperature, such as, 80 °C to 250 °C, or 90 °C to 230 °C, or 100 °C to 210 °C, until the desired reaction has occurred. The molar ratio of the boron compounds to the N-substituted long chain alkenyl succinimides may have ranges including 10:1 to 1:4, or 4:1 to 1:3, or 1:2. An inert liquid may be used in performing the reaction. The liquid may include toluene, xylene, chlorobenzene, dimethylformamide or mixtures thereof.

[0074] The borated polyisobutylene succinimide dispersant may be present at 0.1 to 2 wt %, or 0.2 wt % to 1 wt %.

[0075] Both the borated polyisobutylene succinimide and the polyisobutylene succinimide may have a TBN on an oil free basis of 40 or more, 70 or more, or 85 or more, such as 50 to 130, or 80 to 120, or 90 to 115.

[0076] The total amount of dispersant (from the combination of borated polyisobutylene succinimide and the polyisobutylene succinimide may be present at 2.6 wt % to 8 wt %, or 3.2 wt % to 6 wt %.

[0077] Typically the polyisobutylene succinimide present at. 2.5 wt % to 6 wt %, or 3 wt % to 5 wt %.

[0078] Typically the polyisobutylene succinimide is present in an amount greater than the borated polyisobutylene succinimide. For example the borated polyisobutylene succinimide may comprise less than 50 wt %, or less than 30 wt % of dispersant present. The borated polyisobutylene succinimide may contribute 5 wt % to 25 wt % of dispersant present.

[0079] The polyisobutylene succinimide may contribute more than 50 wt %, or more than 70 wt % of dispersant present. The polyisobutylene succinimide may contribute 75 wt % to 95 wt % of dispersant present.

[0080] The polyisobutylene succinimide dispersant may comprise a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 350 to 5000, or 750 to 3000 or 1550 to 2500.

[0081] Both theborated polyisobutylene succinimide and the 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.

Dispersant Viscosity Modifier

[0082] The lubricating composition of the invention in one embodiment further contains a dispersant viscosity modifier. When present the dispersant viscosity modifier may be present at 0.05 wt % to 1.5 wt %, or 0.1 wt % to 1 wt %, or 0.1 to 0.5 wt %.

[0083] The dispersant viscosity modifier may include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalised with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalised 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. Patents 4,863,623; 6,107,257; 6,107,258; 6,117,825; and US 7,790,661. In one embodiment the dispersant viscosity modifier may include those described in U.S. Patent 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]).

[0084] In one particular embodiment the dispersant viscosity modifier comprises an olefin copolymer further functionalised with a dispersant amine group. Typically, the olefin copolymer is an ethylene-propylene copolymer.

[0085] The olefin copolymer has a number average molecular weight of 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

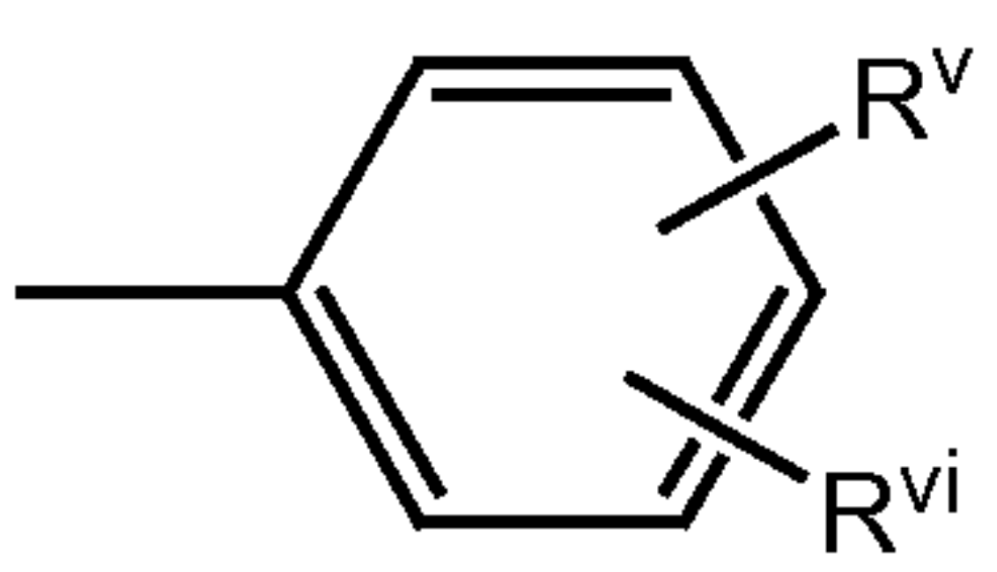
[0086] The dispersant amine group may be prepared/derived from reacting the olefin copolymer (typically, an ethylene-propylene copolymer) with an acylating agent (typically maleic anhydride) and an aromatic amine having a primary or secondary amino group. Typically, the dispersant viscosity modifier may be an ethylene-propylene copolymer acylated with maleic anhydride and reacted with an aromatic amine.

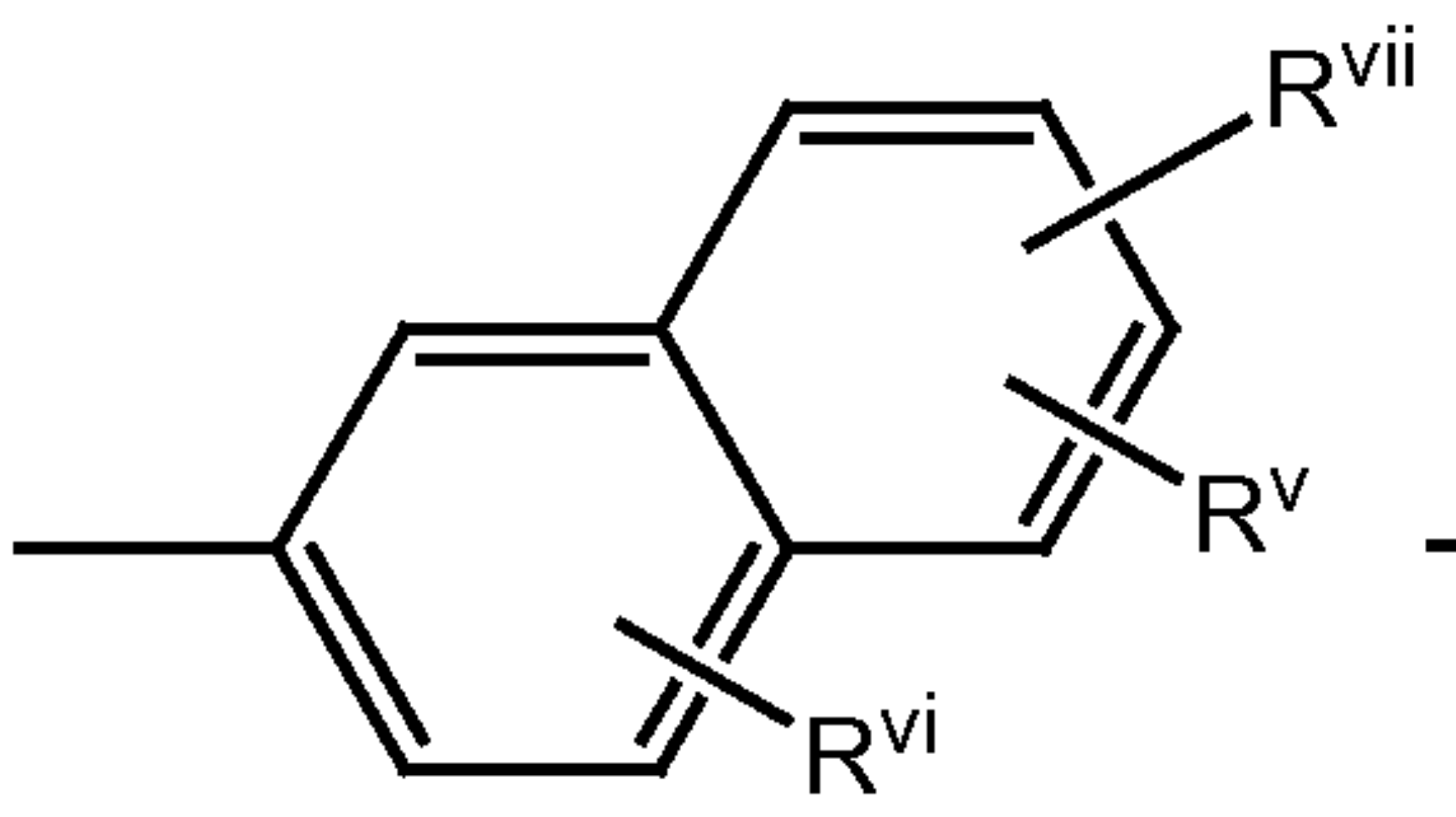
[0087] The formation of a dispersant viscosity modifier is well known in the art. The dispersant viscosity modifier may include for instance those described in U.S. Patent US 7,790,661 column 2, line 48 to column 10, line 38.

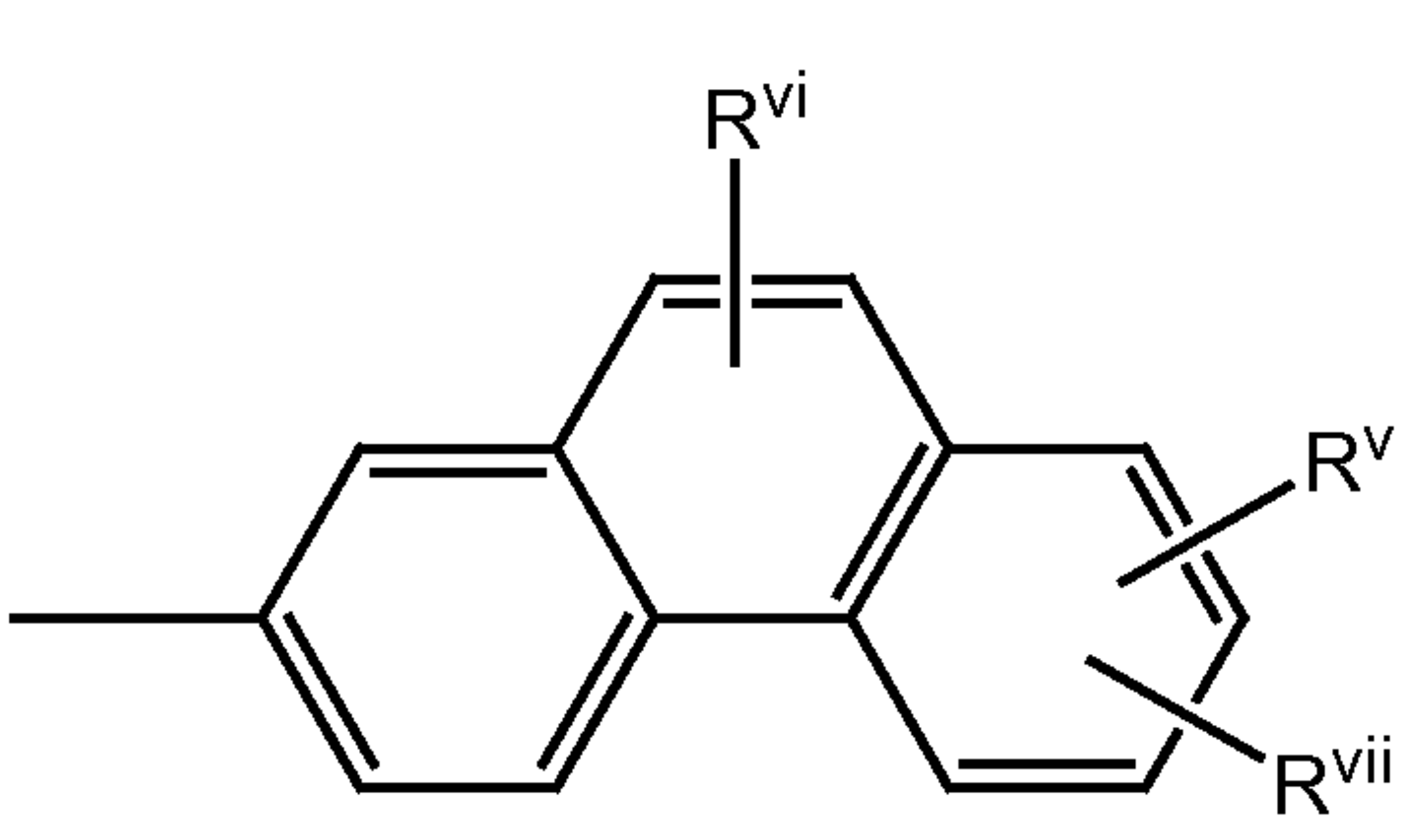
[0088] In one embodiment the dispersant viscosity modifier may be prepared by grafting of an olefinic carboxylic acid acylating agent onto a polymer of 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of C_{3-10} α-monoolefin, and from 0 to 15 mole percent of non-conjugated diene or triene, 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).

[0089] 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 is 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 $-SO_2-$ group where R is 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.

[0090] The aromatic amine of the dispersant viscosity modifier may also include those which can be represented by the general structure NH_2-Ar or T-NH-Ar, where T may be alkyl or aromatic, Ar is an aromatic group, including nitrogen-containing or amino-substituted aromatic groups and Ar groups including any of the following structures:





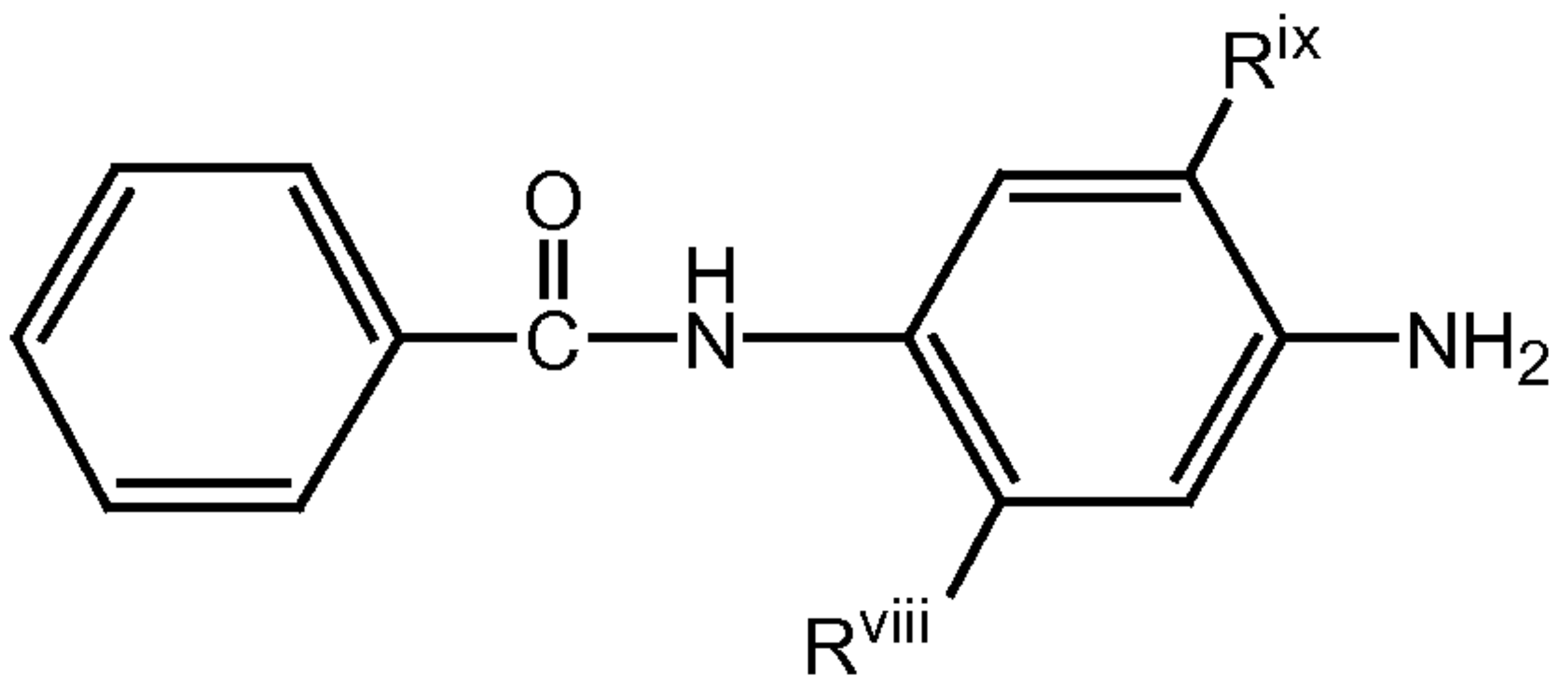


as well as multiple non-condensed or linked aromatic rings. In these and related structures, R^{v}, R^{vi}, and R^{vii} can be independently, among other groups disclosed herein, -H, $-C_{1-18}$ alkyl groups, nitro groups, -NH-Ar, -N=N-Ar, -NH-CO-Ar,

-OOC-Ar, -OOC-C_{1-18} alkyl, -COO-C_{1-18} alkyl, -OH, -O-$(CH_2CH_2\text{-}O)_nC_{1-18}$ alkyl groups, and -O-$(CH_2CH_2O)_n$Ar (where n is 0 to 10).

[0091] 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-nitroaniline, 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-phenylazoaniline, 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.

[0092] Additional aromatic amines and related compounds are disclosed in U.S. Patent 6,107,257 and 6,107,258; some of these include aminocarbazoles, benzoimidazoles, aminoindoles, aminopyrroles, amino-indazolinones, amino-perimidines, mercaptotriazoles, aminophenothiazines, aminopyridines, amino-pyrazines, aminopyrimidines, pyridines, pyrazines, pyrimidines, amino-thiadiazoles, aminothiothiadiazoles, and aminobenzotriaozles. 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:

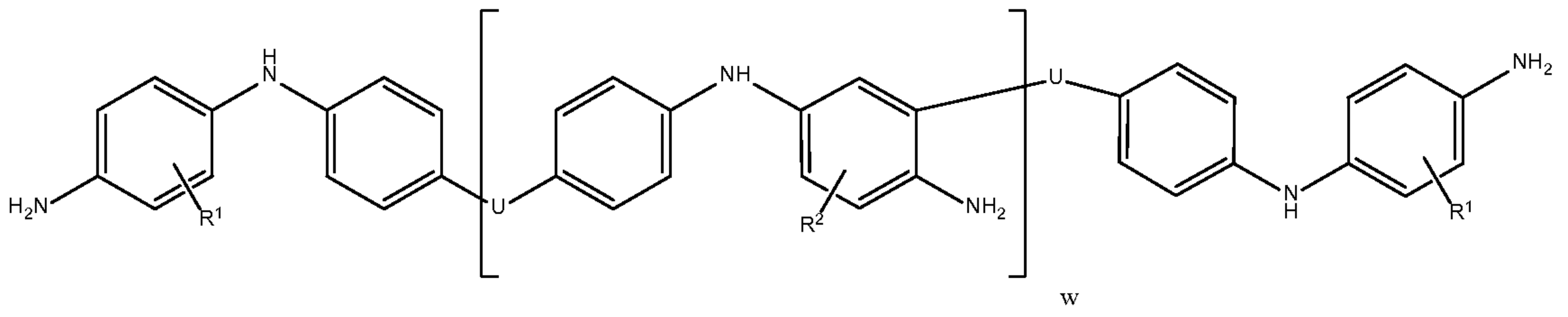


and isomeric variations thereof, where R^{viii} and R^{ix} are independently alkyl or alkoxy groups such as methyl, methoxy, or ethoxy. In one instance, R^{viii} and R^{ix} are both $-OCH_3$ and the material is known as Fast Blue RR [CAS# 6268-05-9].

[0093] In another instance, R^{ix} is $-OCH_3$ and R^{viii} is $-CH_3$, and the material is known as Fast Violet B [99-21-8]. When both R^{viii} and R^{ix} are ethoxy, the material is Fast Blue BB [120-00-3]. U.S. Patent 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 this invention. Suitable aromatic amines include those in which the amine nitrogen is a substituent on an aromatic carboxyclic compound, that is, the nitrogen is not sp^2 hybridized within an aromatic ring.

[0094] 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 $-NH_2$ 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.

[0095] 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 is 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).

[0096] In one embodiment the aromatic amine includes 4-aminodiphenylamine, aldehyde (typically formaldehyde) coupled 4-aminodiphenylamine, nitro-aniline (3- nitro-aniline), disperse orange-3 (DO3), or mixtures thereof.

Other Performance Additives

[0097] 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).

[0098] The lubricating composition of the invention 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, antioxidants, 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.

[0099] The lubricating composition in a further embodiment comprises an antioxidant, wherein the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof. The antioxidants include diarylamines, alkylated diarylamines, hindered phenols, or mixtures thereof. When present the antioxidant is present at 0.1 wt % to 3 wt %, or 0.5 wt % to 2.75 wt %, or 1 wt % to 2.5 wt % of the lubricating composition.

[0100] The diarylamine or alkylated diarylamine may be a phenyl-α-naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnapthylamine, 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 phenylnapthylamines.

[0101] 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-butyl-phenol. 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 US Patent 6,559,105.

[0102] 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 tartrimides; 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.

[0103] 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.

[0104] 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 tartrimides; fatty alkyl tartramides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxylated fatty amines; borated alkoxylated 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 ethoxylated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0105] Friction modifiers may also encompass materials such as sulphurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

[0106] 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.

[0107] The lubricating composition optionally further includes at least one antiwear agent. Examples of suitable antiwear agents include titanium compounds, tartrates, tartrimides, oil soluble amine salts of phosphorus compounds, sulphurised 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) disulphides. The antiwear agent may in one embodiment include a tartrate, or tartrimide as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in US Patent Application 20050198894.

[0108] Another class of additives includes oil-soluble titanium compounds as disclosed in US 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 is a titanium (IV) alkoxide. The titanium alkoxide is 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 is titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide is 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 is oleic acid.

[0109] In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In a further embodiment the titanium (IV) carboxylate is titanium neodecanoate.

[0110] 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.

[0111] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, dimercaptothiadiazole or CS_2 derivatives of dispersants (typically succinimide dispersants), derivative of chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulphurised olefins (such as sulphurised isobutylene), a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, organic sulphides and polysulphides such as dibenzyl-disulphide, bis–(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide 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 dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P_2O_5; and mixtures thereof (as described in US 3,197,405).

[0112] Foam inhibitors that may be useful in the compositions of the invention 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.

[0113] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0114] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0115] 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.

[0116] Seal swell agents include sulfolene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

<ins>Industrial Application</ins>

[0117] 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).

[0118] The lubricating composition may be characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 0.5 wt % to 1.5 wt % or less.

[0119] The lubricating composition may be characterised as having at least one of (i) a sulphur 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 sulphated ash content of 0.5 wt % to 1.5 wt % or less.

[0120] The lubricating composition may be characterised as having a sulphated ash content of 0.5 wt % to 1.2 wt %.

[0121] The lubricating composition may have a total sulphated ash content of 1.2 wt % or less.

[0122] The sulphur 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 sulphur 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 sulphated 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 sulphated ash content may be 0.5 wt % to 1.1 wt % of the lubricating composition.

[0123] In one embodiment the lubricating composition may be characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.15 wt % or less, and (iii) a sulphated ash content of 0.5 wt % to 1.5 wt % or less.

[0124] The lubricating composition may be characterised as having at least one of (i) a sulphur 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 sulphated ash content of 0.5 wt % to 1.5 wt % or less.

[0125] The lubricating composition may be characterised as having a sulphated ash content of 0.5 wt % to 1.2 wt %.

[0126] As used herein TBN values are (total base number) measured by the methodology described in ASTM D4739 (buffer).

[0127] The lubricating composition may be characterized as having a total base number (TBN) content of at least 5 mg KOH/g.

[0128] The lubricating composition may be characterized as having a total base number (TBN) content of 6 to 13 mg KOH/g, or 7 to 12 mg KOH/g.

[0129] 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 20, 30, or 40.

[0130] The internal combustion engine disclosed herein may have a steel surface on a cylinder bore, cylinder block, or piston ring.

[0131] The internal combustion engine may have a surface of steel, or an aluminium alloy, or an aluminium composite.

[0132] Typically the compression-ignition internal combustion engine has a maximum laden mass over 3,500 kg.

[0133] 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

[0134] A series of lubricating compositions are prepared according to Table 1 below. Each composition is formulated to deliver about 1% by weight sulfated ash (ASTM D874) and to have an overall TBN of about 10 (ASTM D2896).

Table 1 – Diesel Lubricant Compositions[1]

	CEX1	EX1	EX2
	10W-30	10W-30	15W-40
Base Oil	Balance to 100%	Balance to 100%	Balance to 100%
Succinimide dispersant[2]	2.0	2.0	2.0
Borated succinimide dispersant3	0.33	0.34	0.34
Aryl amine succinimide dispersant[4]	0.85	0.85	0.85
Overbased calcium sulphonate (metal ratio ~10 TBN = 515)	0	0.58	0.58
"Neutral" calcium sulphonate	0	0.38	0.38

(metal ratio ~1.2)			
Overbased calcium sulphonate (metal ratio ~3 TBN = 160)	0.53	0	0
Overbased magnesium sulphonate	0.44	0.51	0.51
Overbased Calcium sulfur-coupled phenate	0.43	0	0
"Neutral" Calcium sulfur-coupled phenate	0.25	0	0
Magnesium alkylene coupled phenol detergent	0.37	0	0
Aromatic amine dispersant viscosity modifier booster[5]	0.33	0.33	0.33
Secondary ZDDP (C3-6)	1.0	1.0	1.0
Ashless Antioxidants[6]	1.4	1.6	1.6
Other Additives[7]	0.1[8]	0.56	0.56
OCP Viscosity Index Improver	-	0.46	0.74
Pour Point Depressant	0.08	0.08	0.08
Detergent Substrate	1.42	0.83	0.83
Sulfated Ash	1.0	1.0	1.0
TBN	8.8	9.5	9.5

1. *All amounts shown above are in weight percent and are on an oil-free basis unless otherwise noted*
2. *Succinated polyisobutylene (the polyisobutylene has a vinylidene content of less than 25 wt %, and a number average molecular weight of about 2200), aminated with ethylene polyamine (TBN 60)*
3. *Succinated polyisobutylene (the polyisobutylene has a vinylidene content of less than 25 wt %, and a number average molecular weight of about 1000), aminated with ethylene polyamine and borated to provide B:N (wt:wt) of ~0.8*
4. *Succinated polyisobutylene (the polyisobutylene has a vinylidene content of less than 25 wt %, and a number average molecular weight of about 2200), aminated with polyaromatic amine*
5. *OCP(ethylene-propylene copolymer having a number average molecular weight of about 8000) based DVM booster aminated with aromatic amine*
6. *Combination of alkylated diphenylamine, hindered phenol, and sulfurized olefin*
7. *Other additives include low levels of corrosion inhibitors, ashless TBN booster, and anti-foam agents*
8. *No ashless TBN booster*

[0135] The lubricating compositions are evaluated for both durability (i.e. anti-wear) and cleanliness (i.e. deposit control). Durability is measured in the GM 6.5L Roller Follower Wear Test (RFWT), an industry standard wear test for measuring wear in diesel engines where soot accumulates in the lubricant. Deposit control is evaluated in the Caterpillar 1N (CAT 1N) single cylinder engine test, an industry standard test for measuring the ability of diesel lubricants to control oil consumption and prevent/reduce piston deposits especially top groove fill and top land heavy carbon. The results of these tests are summarized in Table 2 below. It is known that lower viscosity grade oils (e.g. 10W-30) are more challenging to maintain durability; to better demonstrate the durability of the lubricating composition of the invention, the lower viscosity grade example (EX 1) was evaluated in the RFWT. The higher viscosity lubricant (EX 2) is evaluated in the CAT 1N engine test.

Table 2 – Wear and Deposit Engine Tests

		CEX1	EX1	EX2
GM 6.5 RFWT	Pin Wear, mils	0.24	0.09	
CAT 1N	Weighted demerits			311
	Top Groove Fill			18
	Top Heavy Carbon			1

[0136] The data demonstrates that the formulation with the combination of low and high metal ratio sulphonates and ashless dispersant reduced wear without having a negative impact on deposit control. The results obtained indicate that the lubricating composition disclosed herein provides at least one of soot, reduced deposit formation, reduced wear and improved cleanliness to a heavy duty diesel engine.

[0137] 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 present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0138] 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.

[0139] 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.

[0140] 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.

[0141] 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.

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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 sulphonate 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 % of a phenolic based detergent,

the total amount of soap delivered by the alkaline earth metal sulphonate (typically calcium sulphonate) is 0.4 to 1 wt % of the lubricating composition, and

the lubricating composition has a sulphated ash content of not more than 1.5 wt %.

2. The method of claim 1, wherein the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 0.5 wt % to 1.5 wt % or less.

3. The method of any preceding claim, wherein the lubricating composition is characterised as having at least one of (i) a sulphur 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 sulphated ash content of 0.5 wt % to 1.5 wt % or less.

4. The method of any preceding claim, wherein the lubricating composition is characterised as having a sulphated ash content of 0.5 wt % to 1.2 wt %.

5. The method of any preceding claim, wherein the lubricating composition is characterized as having a total base number (TBN) content of at least 5 mg KOH/g.

6. The method of any preceding claim, wherein the lubricating composition is characterized as having a total base number (TBN) content of 7 to 10 mg KOH/g.

7. The method of any preceding claim, wherein the total amount of soap delivered by the calcium sulphonate detergents is 0.5 to 0.8 wt % of the lubricating composition.

8. The method of any preceding claim, wherein the lubricating composition further comprises a 80 TBN or lower alkaline earth metal sulphonate detergent having a metal ratio of 1 to 5.

9. The method of claim 8, wherein the ratio of 300 TBN or higher alkaline earth metal sulphonate detergent to 80 TBN or lower alkaline earth metal sulphonate detergent is 80:20 to 20:80, or 70:30 to 30:70, or 65:35 to 35:65.

10. The method of any preceding claim, wherein the 300 TBN or higher alkaline earth metal sulphonate detergent and a metal ratio of 20 to 30, or 22 to 25.

11. The method of any preceding claim, wherein the calcium sulphonate detergent having a metal ratio of 10 to 40 has a TBN of 350 to 500, or 375 to 425.

12. The method of any preceding claim 8 to 10, wherein 80 TBN or lower alkaline earth metal sulphonate detergent having a metal ratio of 1 to 3, or 1 to 2, or 1 to 1.5.

13. The method of any preceding claim 8 to 11, wherein the calcium sulphonate detergent having a metal ratio of 1 to 5 has a TBN of 1 to 80, or 2 to 40, or 5 to 35.

14. The method of any preceding claim, wherein the phenate is a non-sulphur containing phenate, sulphur containing phenate, or a "hybrid" detergent formed with mixed surfactant system, wherein the hybrid is a mixed phenate-salicylate, a sulphonate-phenate, or a sulphonate-phenate-salicylate.

15. The method of any preceding claim further comprising a dispersant viscosity modifier.

16. The method of claim 15, wherein the dispersant viscosity modifier is present at 0.01 wt % to 3 wt %.

17. The method of any preceding claim 15 to 16, wherein the dispersant viscosity modifier is an olefin copolymer further functionalised with a dispersant amine group.

18. The method of claim 17, wherein the olefin copolymer is an ethylene-propylene copolymer.

19. The method of any preceding claim 17 to 18, wherein the olefin copolymer has a number average molecular weight of 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

20. The method of any preceding claim 17 to 19, wherein the dispersant amine group is derived from reacting the olefin copolymer with an acylating agent and an aromatic amine having a primary or secondary amino group.

21. The method of claim 20, wherein the aromatic amine comprises 4-aminodiphenylamine, aldehyde (typically formaldehyde) coupled 4-aminodiphenylamine, nitro-aniline, disperse orange-3 (DO3), or mixtures thereof.

22. The method of any preceding claim 15 to 21, wherein the dispersant viscosity modifier is present at 0.05 wt % to 1.5 wt %, or 0.1 wt % to 1 wt %, or 0.1 to 0.5 wt %.

23. The method of any preceding claim, wherein the lubricating composition further comprises an antioxidant, 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 %, or 0.5 wt % to 2.75 wt %, or 1 wt % to 2.5 wt %.

24. The method of any preceding claim further comprising a phosphorus-containing antiwear agent, typically zinc dialkyldithiophosphate.

25. The method of any preceding claim, wherein the polyisobutylene succinimide is present at 2.5 wt % to 6 wt %, or 3 wt % to 5 wt %.

26. The method of any preceding claim, wherein the borated polyisobutylene succinimide is present at 0.1 to 2 wt %, or 0.2 wt % to 1 wt %.

27. The method of any preceding claim, wherein the polyisobutylene succinimide is present in an amount greater than the borated polyisobutylene succinimide

28. The method of any preceding claim, wherein the borated polyisobutylene succinimide contributes 5 wt % to 25 wt % of dispersant present; and polyisobutylene succinimide contributes 75 wt % to 95 wt % of dispersant present.