US 20170073606A1

(19) **United States**
(12) **Patent Application Publication**
Galic Raguz et al.
(10) **Pub. No.: US 2017/0073606 A1**
(43) **Pub. Date: Mar. 16, 2017**

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

(71) Applicant: **The Lubrizol Corporation**, Wickliffe, OH (US)

(72) Inventors: **Mary Galic Raguz**, Mentor, OH (US); **John G. Loop**, Perry, OH (US); **My Hang T. Truong**, Mentor, OH (US); **William O'Ryan**, Allestree (GB)

(21) Appl. No.: **15/125,393**

(22) PCT Filed: **Feb. 23, 2015**

(86) PCT No.: **PCT/US2015/017027**

§ 371 (c)(1),
(2) Date: **Sep. 12, 2016**

Related U.S. Application Data

(60) Provisional application No. 61/951,628, filed on Mar. 12, 2014.

Publication Classification

(51) **Int. Cl.**
C10M 149/12 (2006.01)
C10M 169/04 (2006.01)

(52) **U.S. Cl.**
CPC ***C10M 149/12*** (2013.01); ***C10M 169/04*** (2013.01); *C10M 2207/026* (2013.01); *C10M 2215/064* (2013.01); *C10M 2215/28* (2013.01); *C10M 2217/06* (2013.01); *C10M 2219/046* (2013.01); *C10M 2223/045* (2013.01); *C10N 2220/021* (2013.01); *C10N 2220/033* (2013.01); *C10N 2230/041* (2013.01); *C10N 2230/52* (2013.01); *C10N 2240/10* (2013.01); *C10N 2230/04* (2013.01); *C10N 2230/10* (2013.01); *C10M 2203/1006* (2013.01)

(57) **ABSTRACT**

The invention provides a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt % soot resulting from operation of the engine, and wherein the lubricant composition comprises an oil of lubricating viscosity, and 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000, and wherein the soot dispersing additive has a shear stability index of 0 to 20.

METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE

FIELD OF INVENTION

[0001] The invention provides a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt % soot resulting from operation of the engine, and wherein the lubricant composition comprises an oil of lubricating viscosity, and 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000, and a shear stability index of 0 to 20.

BACKGROUND OF THE INVENTION

[0002] Equipment manufacturers in recent years having been designing internal combustion engines in ways to assist in the reduction of various greenhouse gases or particulate matter and/or they have been using after treatment devices such as diesel particulate filters, or SCR (selective catalytic reduction). A recent development in engine design has been to incorporate a centrifugal oil mist separator into engines, typically diesel engines (typically having an open or closed crankcase). Centrifugal oil mist separators often become plugged with a deposit (consistency varies from slimy/sludgy to hard-tacky) which, if enough deposits are collected, reduces the efficiency and/or completely disables the device and allows oil to drip out of the engine. This problem is believed to be particularly apparent in heavy duty diesel engines.

SUMMARY OF THE INVENTION

[0003] The present invention allows for an internal combustion engine (typically a compression ignition engine) to have at least one of reduced oil mist separator filter plugging, and reduced deposits such as slimy/sludgy to hard-tacky deposits.

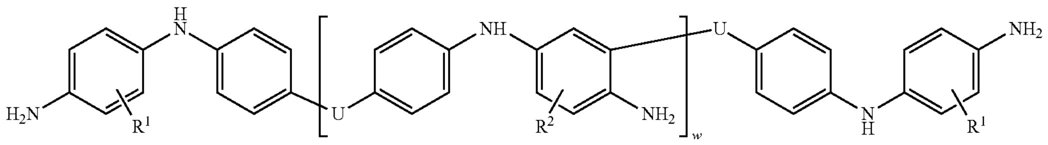
[0004] As used herein reference to the amounts of additives present in the lubricating composition disclosed herein are quoted on an oil free basis, i.e., amount of actives, unless otherwise indicated.

[0005] 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 and novel characteristics of the composition or method under consideration.

[0006] As used herein the expression "compression ignition 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 ignition internal combustion engine, as well as spark assisted compression ignition internal combustion engines.

[0007] The invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt %, or 0.3 wt % to 6 wt % (or typically 0.5 wt % to 4 wt %) soot resulting from operation of the engine, and wherein the lubricant composition comprises an oil of lubricating viscosity, and 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000, and a shear stability index of 0 to 20. Typically the soot dispersing additive may comprise dispersant viscosity modifier derived from a polyolefin with a number average molecular weight of 500 to 20,000, and/or a dispersant comprising an aromatic amine moiety.

[0008] In one embodiment the invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt % soot resulting from operation of the engine, and wherein the lubricant composition comprises an oil of lubricating viscosity, and 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000 and a shear stability index of 0 to 20, and the soot dispersing additive is a dispersant comprising an aromatic amine moiety obtained/obtainable by reacting a carboxylic functionalised polymer (typically a polyisobutylene succinic anhydride) with an amine having at least 4 aromatic groups and an aldehyde (such as formaldehyde). The aromatic amine may be represented by 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).

[0009] in one embodiment the invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt % soot resulting from operation of the engine, and wherein the lubricant composition comprises an oil of lubricating viscosity, and 0.2 wt %

to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000 and a shear stability index of 0 to 20, and wherein the soot dispersing additive is a dispersant viscosity modifier comprising an aromatic amine moiety wherein the dispersant viscosity modifier is an olefin copolymer functionalised with an aromatic moiety, typically olefin copolymer is an ethylene-propylene copolymer.

[0010] In one embodiment the invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt %, or 0.3 wt % to 6 wt % (or typically 0.5 wt % to 4 wt %) soot resulting from operation of the engine, and wherein the lubricant composition comprises:

[0011] an oil of lubricating viscosity,

[0012] a soot dispersing additive, wherein the soot dispersing additive comprises a dispersant viscosity modifier derived from a polyolefin with a number average molecular weight of 500 to 20,000, and has a shear stability index of 0 to 20, and

[0013] a dispersant comprising an aromatic amine moiety, wherein both the dispersant comprising an aromatic amine moiety and the dispersant viscosity modifier are both present with a treat rate of 0.2 wt % to 3.0 wt %, or 0.3 wt % to 2.0 wt %, or 0.4 wt % to 1.5 wt % of the lubricating composition.

[0014] In one embodiment the invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt %, or 0.3 wt % to 6 wt % (or typically 0.5 wt % to 4 wt %) soot resulting from operation of the engine, and wherein the lubricant composition comprises:

[0015] an oil of lubricating viscosity,

[0016] 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000, and a shear stability index of 0 to 20, and an ashless succinimide dispersant different from the soot-dispersing additive, wherein the succinimide dispersant is present at 1 wt % to 8 wt %, or 2 wt % to 6 wt %. Typically the succinimide dispersant comprises a polyisobutylene succinimide, wherein the dispersant has a TBN of at least 40 mg KOH/g and is present in an amount 1.2 wt% to 5 wt% of the lubricating composition.

[0017] In one embodiment the invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt %, or 0.3 wt % to 6 wt % (or typically 0.5 wt % to 4 wt %) soot resulting from operation of the engine, and wherein the lubricant composition comprises:

[0018] an oil of lubricating viscosity,

[0019] 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000, and a shear stability index of 0 to 20,

[0020] an overbased sulfonate detergent present at 0.01 wt % to 0.9 wt %, or 0.05 wt % to 0.8 wt %, or 0.1 wt % to 0.7 wt %, or 0.2 wt % to 0.6 wt %.

[0021] In one embodiment the invention relates to a method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt %, or 0.3 wt % to 6 wt % (or typically 0.5 wt % to 4 wt %) soot resulting from operation of the engine, and wherein the lubricant composition comprises:

[0022] an oil of lubricating viscosity, 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000, and a shear stability index of 0 to 20,

[0023] an ashless succinimide dispersant different from the soot-dispersing additive, wherein the succinimide dispersant is present at 1 wt % to 8 wt %, or 2 wt % to 6 wt, and

[0024] an overbased sulfonate detergent present at 0.01 wt % to 0.9 wt %, or 0.05 wt % to 0.8 wt %, or 0.1 wt % to 0.7 wt %, or 0.2 wt % to 0.6 wt %.

[0025] The internal combustion may have an open or closed crankcase, typically an open crankcase. Both open and closed crankcase ventilation are known in the art. For example open crankcase ventilation prevents build-up of pressure in the crankcase by externally venting blow-by emission combustion products that include hydrocarbons, carbon monoxide, NOx and particulate matter. In closed crankcase ventilation (CCV) systems, crankcase gases are typically filtered to remove oil mist and other particulates and then routed back into the intake system.

[0026] Typically the internal combustion engine of the present invention may have a closed crankcase ventilation.

[0027] The heavy duty vehicle (HDV) containing the internal combustion engine of the present invention may have a laden mass (sometimes referred to as gross vehicle weight rating (GVWR)) of over 2700 kg (or 6000 USA pounds), or over 2900 kg, or over 3000 kg, or over 3300 kg, or over 3500 kg, or over 3700 kg, or over 3900 kg (or 8500 USA pounds). Typically the upper limit on the laden mass or

[0028] GVWR is set by national government and may be 10000 kg, or 9000 kg, or 8000 kg, or 7500 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 is for an off-highway vehicle.

[0029] The vehicle containing the internal combustion engine of the present invention having a laden mass of over 2700 kg (or 3,500 kg) may be a heavy duty diesel engines 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.

[0030] Typically the internal combustion engine may be a diesel engine suitable for powering a vehicle having a laden mass over 2,700 kg.

[0031] The centrifugal oil mist separator typically rotates at 2500 to 10000, or 4000 to 8000, or 5000 to 7000 rpm.

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

[0033] There is a distinct difference between passenger car and heavy duty diesel engines. They differ in size from not more than 2610 kg to over 3500 kg GVWR respectively, which means that engines of both types will experience significantly different operating conditions such as load, oil temperatures, duty cycles 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 lubricants 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.

[0034] In another embodiment the invention provides for a method of operating a centrifugal oil mist separator wherein the centrifugal oil mist separator is provided with a lubricant for separation comprising 0.1 wt % to 8 wt %, or 0.3 wt % to 6 wt % (or typically 0.5 wt % to 4 wt %) of soot, and a lubricating composition disclosed herein.

DETAILED DESCRIPTION OF THE INVENTION

[0035] The present invention provides a method for lubricating an internal combustion engine as disclosed above.

[0036] Oils of Lubricating Viscosity

[0037] 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 W02008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in U.S. 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 U.S. Patent Application 2010/197536, see [0075] to [0076]).

[0038] Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized 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.

[0039] 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 U.S. Pat. No. 7,285,516 (see column 11, line 64 to column 12, line 10).

[0040] In one embodiment the oil of lubricating viscosity may be an API Group I to III mineral oil, a Group IV synthetic oil, or a Group V napthethnic or ester synthetic oil, or mixtures thereof. In one embodiment the oil of lubricating viscosity may be an API Group II, Group III mineral oil, or a Group IV synthetic oil, or mixtures thereof.

[0041] 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.

[0042] 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.

Soot Dispersing Additive

[0043] The soot dispersing additive may have a shear stability index of 0 to 20, or 0 to 15, or 0 to 10, or 0 to 5 as measured by dissolving an appropriate amount of the additive in a 6.0 to 6.1 mm/s^2 or cSt (measured at 100° C. according to ASTM D445) Group I or Group II mineral oil to prepare a 9-13 mm^2/s or cSt solution and testing the solution in the Orbahn shear test (ASTM D6278).

[0044] The soot dispersing additive may be present at 0.2 wt % to 3 wt %, or 0.2 wt % to 2.5 wt %, or 0.3 wt % to 1.4 wt % of the lubricating composition.

[0045] The soot dispersing additive may have a shear stability index of 0 to 10 and be present at 0.2 wt % to 2.5 wt %, or 0.3 wt % to 1.4 wt %.

[0046] The soot dispersing additive may have a shear stability index of 0 to 5 and be present at 0.2 wt % to 2.5 wt %, or 0.3 wt % to 1.4 wt %.

[0047] The soot dispersing additive of the present invention may be dispersant viscosity modifier derived from a polyolefin with a number average molecular weight of 500 to 20,000, comprising an aromatic amine moiety, or a dispersant comprising an aromatic amine moiety.

[0048] In one embodiment the lubricating composition comprises dispersant viscosity modifier comprising an aromatic amine moiety, and a dispersant comprising an aromatic amine moiety.

[0049] When a dispersant viscosity modifier comprising an aromatic amine moiety of the invention, and a dispersant comprising an aromatic amine moiety are both present the treat rate of each may be 0.2 wt % to 3.0 wt %, or 0.3 wt % to 2.0 wt %, or 0.4 wt % to 1.5 wt % of the lubricating composition.

Dispersant Viscosity Modifier

[0050] The lubricating composition of the invention contains a dispersant viscosity modifier. 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 %.

[0051] 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.

[0052] In one particular embodiment the dispersant viscosity modifier comprises an olefin copolymer further functionalized with a dispersant amine group. Typically, the olefin copolymer is an ethylene-propylene copolymer.

[0053] The olefin copolymer has a number average molecular weight of 5000 to 20,000, or 6000 to 18,000, or 7000 to 15,000.

[0054] The olefin copolymer may have a shear stability index of 0 to 20, or 0 to 10, or 0 to 5 as measured by the Orbahn shear test (ASTM D6278) as described above.

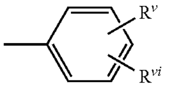
[0055] The dispersant viscosity modifier may be prepared/derived from reacting the olefin copolymer (typically, an ethylene-propylene copolymer) with an acylating agent (typically maleic anhydride) and an aromatic amine having at least one primary or secondary amino group. The reaction with an acylating agent may be conducted in the presence of a peroxide initiator and subsequently reacting the acylated olefin copolymer with an aromatic amine. The dispersant viscosity modifier may be prepared in the presence of, or in the substantial absence of, an organic solvent, typically an API Group I or Group II or Group III mineral oil. API Group IV and V oils can also be used.

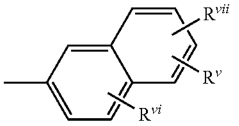
[0056] The formation of a dispersant viscosity modifier is well known in the art. The dispersant viscosity modifier may include for instance those described in U.S. Patent U.S. Pat. No. 7,790,661 column 2, line 48 to column 10, line 38.

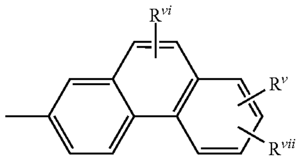
[0057] In one embodiment the dispersant viscosity modifier may be prepared by grafting of an olefinic carboxylic acid acylating agent onto a polymer of 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of C_{3-10} α-monoolefin, and from 0 to 15 mole percent of non-conjugated diene or triene, said polymer having an average molecular weight ranging from 5000 to 20,000, and further reacting said grafted polymer with an amine (typically an aromatic amine).

[0058] 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 to 20,000; and (b) an amine component comprising at least one aromatic amine (from which the aromatic moiety is derived from) 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.

[0059] 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:



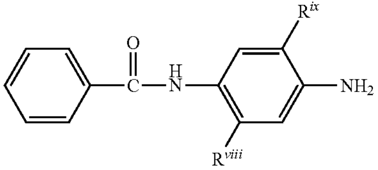




as well as multiple non-condensed or linked aromatic rings. In these and related structures, R^{v}, R^{vi}, and R^{vii} can be independently, among other groups disclosed herein, —H, —C_{1-18} alkyl groups, nitro groups, —NH—Ar, —N═N—Ar, —NH—CO—Ar, —OOC—Ar, —OOC—C_{1-18} alkyl, —COO—C_{1-18} alkyl, —OH, —O—$(CH_2CH_2—O)_nC_{1-18}$ alkyl groups, and —O—$(CH_2CH_2O)_nAr$ (where n is 0 to 10).

[0060] 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-amino acetanilide (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.

[0061] Additional aromatic amines and related compounds are disclosed in U.S. Pat. Nos. 6,107,257 and6,107,258; some of these include aminocarbazoles, benzoimidazoles, aminoindoles, aminopyrroles, amino-indazolinones, amino-perimidines, mercaptotriazoles, aminophenothiazines, aminopyridines, amino-pyrazines, aminopyrimidines, pyridines, pyrazines, pyrimidines, aminothiadiazoles, 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:

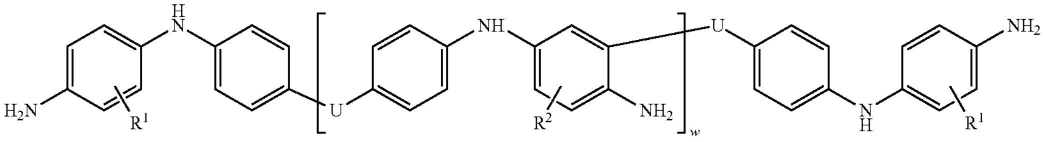


and isomeric variations thereof, where R^{viii} and R^{ix} are independently alkyl or alkoxy groups such as methyl, methoxy, or ethoxy. In one instance, R^{viii} and R^{ix} are both —OCH$_3$ and the material is known as Fast Blue RR [CAS#6268-05-9].

[0062] 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. 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 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.

[0063] 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.

[0064] 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 (1):



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);

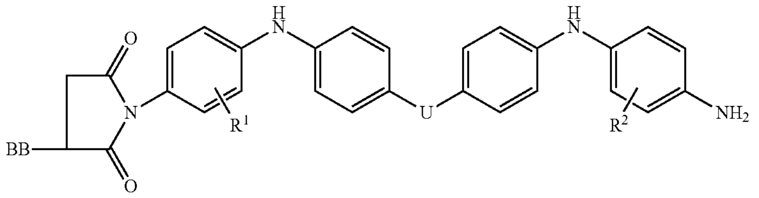
U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U is aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and

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

[0065] In one embodiment the aromatic amine includes 4-aminodiphenylamine, aldehyde (typically formaldehyde) coupled 4-aminodiphenylamine, 3- nitro-aniline, disperse orange-3 (4-4-nitrophenyl-azo-aniline, 4-nitrophenylazoaniline, or DO3), or mixtures thereof.

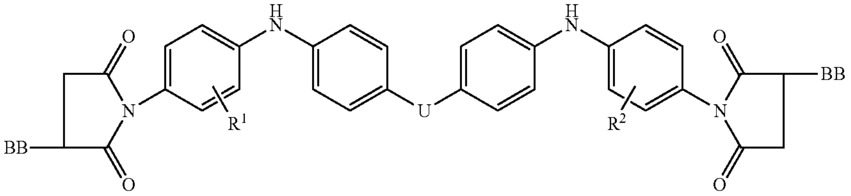
[0066] The soot dispersing additive may be a dispersant comprising an aromatic amine moiety obtained/obtainable by reacting a carboxylic functionalised polymer known in the art (typically a polyisobutylene succinic anhydride) with an amine having at least 4 aromatic groups (typically an aldehyde (such as formaldehyde coupled 4-aminodiphenylamine). The soot dispersing additive of this type is described for example in U.S. Pat. No. 8,557,753. The soot dispersing additive of this type may have a shear stability index of 0 to 10, or 0 to 5 as measured by the Orbahn shear test (ASTM D6278).

[0067] The resultant product of reacting the carboxylic functionalised polymer (typically a polyisobutylene succinic anhydride) with an amine having at least 4 aromatic groups may be represented by the formulae:



or

-continued



wherein independently 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; BB is a polymer backbone and may be polyisobutylene, or copolymers of polyolefins (in particular ethylene-alphaolefins such as ethylene-propylene copolymers). BB may be substituted with one succinimide group as is shown in formulae above, or it may be substituted by multiple succinimide groups.

[0068] In addition to formulae above, additional structures may also be formed including trimers, tetramers, highermers or mixtures thereof.

[0069] When BB is 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.

[0070] When BB is other than polyisobutylene, and has maleic anhydride (or other carboxylic acid functionality) grafted thereon, one or more of the grafted maleic anhydride groups is a succinimide of the amine of the invention. The number of succinimide groups may be 1 to 40, or 2 to 40, or 3 to 20.

[0071] When the soot dispersing additive is derived from 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 have, that is, 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.

[0072] When the soot dispersing additive is derived from polyisobutylene succinic anhydride, the polyisobutylene succinic anhydride may be formed by reactions known in the art such as by an "ene" reaction, or a "Diels-Alder" reaction (typically obtained/obtainable by Diels Alder reaction).

[0073] In one embodiment the aromatic amine may be a reaction product of isatoic anhydride and 4-aminodiphenylamine) that can be reacted with a carboxylic functionalised polymer. The carboxylic functionalised polymer may include polyisobutylene succinic anhydride, maleic anhydride-styrene copolymers, esters of maleic anhydride-styrene copolymers, (alpha-olefin maleic anhydride) copolymers; maleic anhydride-grafted styrene-ethylene-alpha olefin polymers; polymethacrylates; polyacrylates; polyhydroxycarboxylic acids (including polyhydroxystearic acid); maleic anhydride graft copolymers of (i) hydrogenated alkenyl aryl conjugated diene copolymers (in particular hydrogenated copolymers of styrene-butadiene), (ii) polyolefins grafted with maleic anhydride (in particular ethylene-propylene copolymers), or mixtures thereof. Typically the aromatic amine may be a reaction product of isatoic anhydride and 4-aminodiphenylamine) that can be reacted with either polyisobutylene succinic anhydride polyolefins grafted with maleic anhydride (in particular ethylene-propylene copolymers), or mixtures thereof. A more detailed description of this aromatic amine is provided in U.S. Pat. No. 8,637,437.

Overbased Sulfonate Detergent

[0074] In one embodiment the lubricating composition comprises an overbased sulfonate detergent. The overbased sulfonate detergent may be present at 0.01 wt % to 0.9 wt %, or 0.05 wt % to 0.8 wt %, or 0.1 wt % to 0.7 wt %, or 0.2 wt % to 0.6 wt %.

[0075] The sulfonate 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.

[0076] 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.

[0077] In one embodiment the hydrocarbyl-substituted sulfonic acid may include polypropene benzenesulfonic acid and C_{16}-C_{24} alkyl benzenesulfonic acid, or mixtures thereof.

[0078] Overbased sulfonates typically have a total base number of 250 to 600, or 300 to 500. Overbased detergents are known in the art. In one embodiment the sulfonate detergent may be a predominantly linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 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.

[0079] Overbased detergents are known in the art. 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. The term "metal ratio is also explained in standard textbook entitled "Chemistry and Technology of Lubricants", Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, page 219, sub-heading 7.25. Typically the overbased sulfonate of the present invention may have a metal ratio of 3.5:1 to 40:1, or 5:1 to 30:1, or 12:1 to 25:1. Typically the overbased sulfonate of the present invention has a TBN of 300 to 500 and a metal ratio of 12:1 to 25:1. In different embodiment the overbased sulfonate detergent has a metal ratio of 12 to less than 20, or 12 to 18, or 20 to 30, or 22 to 25.

[0080] In one embodiment the overbased sulfonate detergent comprises an overbased calcium sulfonate, a sodium sulfonate, a magnesium sulfonate, or mixtures thereof. Typically the overbased sulfonate is/comprises a calcium sulfonate.

[0081] In one embodiment the overbased sulfonate detergent comprises a calcium sulfonate detergent having a metal ratio of 18 to 40 has a TBN of 300 to 500, or 325 to 425.

Other Performance Additives

[0082] 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).

[0083] The lubricating composition of the invention optionally comprises other performance additives. The other performance additives include at least one of metal deactivators, viscosity modifiers (other than the soot dispersing additive of the present invention), detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants (other than those of the present invention), 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.

[0084] In one embodiment the invention provides a lubricating composition further comprising an overbased metal-containing detergent in addition to the overbased sulfonate detergent defined as an essential feature of the present invention. The metal of the metal-containing detergent may be zinc, sodium, calcium, barium, or magnesium. Typically the metal of the metal-containing detergent may be sodium, calcium, or magnesium.

[0085] The overbased metal-containing detergent may be chosen from non-sulfur containing phenates, sulfur containing phenates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof. The overbased detergent may be borated with a borating agent such as boric acid.

[0086] The overbased metal-containing detergent may also include "hybrid" detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g. phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described; for example, in U.S. Pat. Nos. 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a "hybrid sulfonate/phenate detergent is employed, the "hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0087] Typically, an overbased metal-containing detergent may be a zinc, sodium, calcium or magnesium salt of a phenate, sulfur containing phenate, salixarate or salicylate. Overbased salixarates, phenates and salicylates typically have a total base number of 180 to 450 TBN.

[0088] Typically, the overbased metal-containing detergent may be a calcium or magnesium an overbased detergent.

[0089] In another embodiment the lubricating composition further comprises a calcium phenate overbased detergent having a TBN of 200 to 275.

[0090] In one embodiment the lubricating composition further comprises 0.01 wt % to 2 wt %, or 0.1 to 1 wt % of a detergent different from the overbased sulfonate detergent, wherein the further detergent is chosen from non-sulfur containing phenates, sulfur containing phenates, sulfonates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof.

[0091] In one embodiment the lubricating composition further comprises a "hybrid" detergent formed with mixed surfactant systems including phenate and/or sulfonate components, e.g. phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, or sulfonates/phenates/salicylates.

[0092] 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.

[0093] 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.

[0094] 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.

[0095] The lubricating composition may in a further embodiment include a dispersant (different to the soot dispersing additive), or mixtures thereof. The dispersant may be a succinimide dispersant, a Mannich dispersant, a succinamide dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof. In one embodiment the dispersant may be present as a single dispersant. In one embodiment the dispersant may be present as a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0096] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof.

[0097] In one embodiment the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be chosen from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene-hexamine, polyamine still bottoms, and mixtures thereof.

[0098] In one embodiment the dispersant may be a polyolefin succinic acid ester, amide, or ester-amide. For instance, a polyolefin succinic acid ester may be a polyisobutylene succinic acid ester of pentaerythritol, or mixtures thereof. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and a polyamine as described above.

[0099] The dispersant may be an N-substituted long chain alkenyl succinimide.

[0100] An example of an N-substituted long chain alkenyl succinimide is polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. 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.

[0101] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment the post-treated dispersant is borated. In one embodiment the post-treated dispersant is reacted with dimercaptothiadiazoles. In one embodiment the post-treated dispersant is reacted with phosphoric or phosphorous acid. In one embodiment the post-treated dispersant is reacted with terephthalic acid and boric acid (as described in US Patent Application US2009/0054278.

[0102] When present, the dispersant may be present at 0.01 wt % to 20 wt %, or 0.1 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 6 wt %, or 1 to 3 wt % of the lubricating composition.

[0103] In one embodiment the lubricating composition disclosed herein further comprises an ashless dispersant comprising a succinimide dispersant different from the soot-dispersing additive of the invention, wherein the succinimide dispersant has a TBN of at least 40 mg KOH/g, and said dispersant is present at 1.2 wt % to 5 wt %, or 1.8 wt % to 4.5 wt % of the lubricating composition.

[0104] The 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 2500.

[0105] 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.

[0106] 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.

[0107] 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.

[0108] Friction modifiers may also encompass materials such as sulfurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

[0109] 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.

[0110] 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, sulfurised 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 thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides. 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.

[0111] Another class of additives includes oil-soluble titanium compounds as disclosed in U.S. Pat. No. 7,727,943 and U.S.2006/0014651. 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.

[0112] In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In a further embodiment the titanium (IV) carboxylate is titanium neodecanoate.

[0113] 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.

[0114] Extreme Pressure (EP) agents that are soluble in the oil include sulfur- and chlorosulfur-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; sulfurized olefins (such as sulfurized isobutylene), a hydro carbyl-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; phosphosulfurized 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, dicyclo-hexyl 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 U.S. Pat. No. 3,197,405).

[0115] 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.

[0116] Other viscosity modifiers may include a block copolymer comprising (i) a vinyl aromatic monomer block and (ii), a conjugated diene olefin monomer block (such as a hydrogenated styrene-butadiene copolymer or a hydrogenated styrene-isoprene copolymer), a polymethacrylate, an ethylene-alpha olefin copolymer, a hydrogenated star polymer comprising conjugated diene monomers such as butadiene or isoprene, or mixtures thereof.

[0117] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, fumarate ester-vinyl acetate copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0118] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0119] 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.

[0120] Seal swell agents include sulfolene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

INDUSTRIAL APPLICATION

[0121] In one embodiment the oil mist separator may be driven by an oil turbine. This, in turn, is driven by pressurized lubricant oil normally available in diesel engines. This turbine, fitted in the bottom housing of the unit, spins the centrifugal rotor. There is a separator drain that feeds the oil back to the sump. The centrifugal rotor may carry a number of conical discs, stacked on top of each other, and it is here that the separation of oil mist from the blow-by gases takes place, and where soot may accumulate during engine operation. As the disc stack rotates, the dirty crankcase gas is subject to centrifugal acceleration that amounts to 25 000 m/s^2 (82 000 ft/s^2).

[0122] Without being bound by theory, these centrifugal forces, are believed to correspond to 2 500 times the effect of the earth's gravity, make the oil droplets separate out from the gas. The oil is then thrown off the edges of the discs and onto the inside wall of the oil mist separator housing, from where it runs via the drain outlet back to the sump. The clean gas, on the other hand, passes to the outlet of the unit and then on into the inlet manifold of the engine. In addition to being a separator unit, the disc stack works as a fan, extracting the blow-by gas from the crankcase and avoiding pressure drop across the unit. An internal pressure control valve ensures that the crankcase pressure is always kept within a suitable working range, despite any pressure variations in the inlet manifold. An oil mist separator of this type is known in the art and is sold commercially under the Alfdex® trademark.

[0123] 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).

[0124] The lubricating composition may have a total sulfated ash content of 1.2 wt % or less.

[0125] 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.

[0126] 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.

[0127] 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.

[0128] The lubricating composition may be characterized as having a sulfated ash content of 0.5 wt % to 1.2 wt %.

[0129] As used herein TBN values are (total base number) measured by the methodology described in D4739 (buffer).

[0130] The lubricating composition may be characterized as having a total base number (TBN) content of at least 5 mg KOH/g.

[0131] 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.

[0132] 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.

[0133] The internal combustion engine disclosed herein may have a steel surface on a cylinder bore, cylinder block, or piston ring.

[0134] The internal combustion engine may have a surface of steel, or an aluminum alloy, or an aluminum composite.

[0135] Typically the vehicle powered by the compression-ignition internal combustion engine of the present invention has a maximum laden mass over 3,500 kg.

[0136] 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

[0137] Soot Dispersing Molecule A—Polyisobutylene-based soot dispersant (EXA). 500 mL of 2M hydrochloric acid is added to a one-liter 4-neck flask equipped with an overhead stirrer, thermowell, addition funnel with nitrogen line, and condenser. 184.2 g of 4-aminodiphenylamine (also described as N-phenyl-p-phenylenediamine) is added, and the flask is heated to 75° C. The addition funnel is then charged with 40.5 g of a 37% formaldehyde solution and the solution is added drop-wise to the flask over a period of 30 minutes. The flask is maintained at 100° C. for 4 hours. The flask is then cooled to ambient temperature. 80 g of a 50/50 wt/wt solution of sodium hydroxide in water is added over 30 minutes. At the end of the reaction, a solid product is obtained via filtration. This material may be described as a hydrocarbyl-coupled polyaromatic amine.

[0138] A three-liter, 4-neck flask equipped with an overhead stirrer, thermowell, subsurface inlet with nitrogen line, and Dean-Stark trap with condenser is charged with polyisobutylene succinic anhydride (1270.0 g) (where the polyisobutylene has a number average molecular weight of 2000) and diluent oil (1400.1 g). The flask is heated to 90° C. The hydrocarbyl-coupled polyaromatic amine described above (442.0 g) is added slowly. The temperature is then raised to 110° C. and held until any residual water is removed. The temperature is then raised to 160 ° C. and held for 10 hours. To the flask is added a portion of a diatomaceous earth filter aid, and then flask contents are filtered through a second portion of the diatomaceous earth filter aid. The resultant product is a dark oil with a nitrogen content of 0.65 wt %

[0139] A series of 15W-40 diesel lubricating compositions are prepared according to Table 1 below. The compositions comprise a cross-section of soot-dispersing molecules to evaluate the tendency to plug the centrifugal oil mist separator.

TABLE 1

Diesel Lubricant Compositions[1]

	EX1	EX2	EX3	EX4	CEX5[7]
Group II Base Oil	Balance to 100%				
Low Mn D-OCP[2]	1.00	0.13	0.1	0.1	0
High Mn D-OCP[3]	0	0	0	0	0.85
EXA-PIB-based soot dispersant[4]	0	0	1.5	1.5	0
Succinimide dispersant[5]	4.28	4.10	2.13	2.17	4.4[8]
Overbased Ca sulfonate	0.90	0.90	1.12	0.74	0.7[9]
Overbased Mg sulfonate	0	0	0	0.31	0.3[9]
Overbased Ca sulfur-coupled phenate	0.81	0.81	0.63	0.68	N/A
Mg sulfur-free phenate	0	0	0	0.4	0
Ashless Antioxidants[6]	1.83	1.23	1.40	1.40	1.5
Secondary ZDDP (C3-6)	1.0	1.0	0.86	0.86	1.0
OCP VI Improver	0.50	0.70	0.80	0.82	0
% Calcium (ppm)	2600	2300	2440	1730	1500
% Magnesium (ppm)	30	0	0	535	400
% Phosphorus (ppm)	1200	1100	960	960	1150
% Molybdenum (ppm)	0	0	0	0	90
% Boron (ppm)	50	0	40	48	535

[1] All amounts shown above are in weight percent and are on an oil-free basis unless otherwise noted and include low levels of other additives including corrosion inhibitors, pour point depressants, ashless TBN boosters, and foam inhibitors

[2] OCP (8000 Mn) based DVM booster aminated with aromatic amine (Available as Lubrizol ® 6586H)

[3] OCP (64k Mn) based DVM aminated with 4-amino-diphenylamine (available as Afton HiTec ® 5777)

[4] Soot dispersing molecule A as above

[5] Boron containing and/or boron-free succinimide dispersants

[6] Combination of alkylated diphenylamine, hindered phenol, and sulfurized olefin

[7] Commercial CJ-4 lubricant available as Chevron DELO 400LE

[8] PIBsuccinimide dispersant with a mixture of aromatic amine and polyetheramine head-groups

[9] Estimated

[0140] The lubricating compositions are evaluated for oil mist separator fouling and soot handling. Oil mist separator compatibility was evaluated in diesel trucks equipped with 2010EC DD15 engines manufactured by Detroit Diesel Corporation (DDC). The engines were equipped with Alfdex® centrifugal oil mist separators. The oils were evaluated in field trials ranging from 250,000 miles to nearly 600,000 miles. All of the oil mist separator (OMS) units were inspected after the field trials were completed and rated for sludge deposit formation and drain hole plugging. OMS sludge deposit rating is assigned as follows:

Rating Number	Description	Impact
0	No sludge	No problem
1	Beginning of sludge deposits	Reliability not endangered
2	Light sludge	Reliability not endangered
3	Severe sludge, no drain holes plugged	Reliability not endangered
4	2 of 4 drain holes plugged	Separator efficiency endangered
5	All drain holes plugged with sludge	100% oil carry over to T/C inlet

[0141] Soot handling ability may be measured in fired engine tests (e.g. Mack T 11 engine test) as well as in bench tests. The lubricants are evaluated for Mack T-11 performance by methodology described in ASTM standard procedure D7156. Typically better results are obtained for samples having higher soot content at the point of 12 mm^2/s (cSt) viscosity increase. For API CJ-4 lubricants, the passing limits require the lubricant to contain at least 3.5 weight % soot at 4 mm^2/s increase in kinematic viscosity, to contain at least 6.0 weight % soot at 12 mm^2/s increase in viscosity, and to contain at least 6.7 weight % soot at 15 mm^2/s increase in viscosity all at 100° C. per the test method. The results of these tests are summarized in Table 2 below.

TABLE 2

Oil Mist Separator Compatibility and T-11 Soot Handling

	EX1	EX2	EX3	EX4	CEX5
OIL MIST SEPARATOR					
NO. of UNITS	5	5	1	1	5
AVE. MILES on TEST	269,700	556,800	310,000	378,100	256,000
AVERAGE RATING	1.9	1.9	1.0	1.0	4.0
BLOCKED HOLES	0.0	0.0	0.0	0.0	2.2
MACK T-11 ENGINE TEST					
SOOT @ 4⑦ cSt		4.82%	5.65%	6.28%	
SOOT @ 12 K cSt		7.41%	7.08%	6.83%	
SOOT @ 15K cSt		7.84%	7.43%	7.15%	

⑦ indicates text missing or illegible when filed

[0142] The results obtained indicate that the lubricating composition disclosed herein prevents filter plugging in the oil mist separator and provides superior soot handling capability.

[0143] 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.

[0144] 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.

[0145] 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.

[0146] 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 U.S. 2010-0197536.

[0147] 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.

1-35. (canceled)

36. A method of lubricating an internal combustion engine equipped with a centrifugal oil mist separator, wherein the lubricant contains 0.1 wt % to 8 wt % soot resulting from operation of the engine, and wherein the lubricant composition comprises an oil of lubricating viscosity, and 0.2 wt % to 3 wt % of a soot dispersing additive, wherein the soot dispersing additive comprises a polymer chain having a number average molecular weight of 500 to 20,000 and a shear stability index of 0 to 20.

37. The method of claim **36**, wherein the lubricating composition has (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 %.

38. The method of claim **36**, wherein the lubricating composition has at least one of (i) a sulfur content of 0.2 wt % to 0.4 wt %, (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 %.

39. The method of claim **38**, wherein the lubricating composition has a sulfated ash content of 0.5 wt % to 1.2 wt %.

40. The method of claim **36**, wherein the lubricating composition has a total base number (TBN) content of at least 5 mg KOH/g.

41. The method of claim **40**, wherein the lubricating composition has a total base number (TBN) content of 6 to 13 mg KOH/g.

42. The method of claim **36**, wherein the vehicle powered by a compression-ignition internal combustion engine has a maximum laden mass over 3,500 kg.

43. The method of claim **36**, wherein the soot dispersing additive has a shear stability index of 0 to 10.

44. The method of claim **36**, wherein the soot dispersing additive is selected from the group consisting of a dispersant viscosity modifier comprising an aromatic amine moiety, a dispersant comprising an aromatic amine moiety and mixtures thereof.

45. The method of claim **44**, wherein the soot dispersing additive comprises a dispersant viscosity modifier comprising an aromatic amine moiety wherein the dispersant viscosity modifier is an olefin copolymer functionalised with an aromatic moiety.

46. The method of claim **45**, wherein the olefin copolymer has a shear stability index of 0 to 10.

47. The method of claim **45**, wherein the dispersant viscosity modifier is derived from reacting the olefin copolymer with an acylating agent and an aromatic amine having a primary or secondary amino group.

48. The method of claim **47**, wherein the aromatic amine is selected from the group consisting of 4-aminodiphenylamine, aldehyde coupled 4-aminodiphenylamine, nitroaniline, 4-nitrophenylazoaniline, and mixtures thereof.

49. The method of claim **36**, wherein the soot dispersing additive is a dispersant comprising an aromatic amine moiety obtained by reacting a carboxylic functionalised polymer with an amine having at least 4 aromatic groups and an aldehyde.

50. The method of claim **36**, wherein the lubricating composition further comprises a phenolic or an aminic antioxidant or mixtures thereof, and wherein the antioxidant is present at 0.1 wt % to 3 wt %.

51. The method of claim **36**, wherein the lubricating composition further comprises an overbased sulfonate detergent present at 0.01 wt % to 0.9 wt %.

52. The method of claim **51**, wherein the overbased sulfonate detergent has a metal ratio of 12 to less than 20.

53. The method of claim **51**, wherein the overbased sulfonate detergent has a metal ratio of 20 to 30.

54. The method of claim **51**, wherein the lubricating composition further comprises 0.01 wt % to 2 wt % of a detergent different from the overbased sulfonate detergent, wherein the further detergent is selected from the group consisting of borated and non-borated non-sulfur containing phenates, borated and non-borated sulfur containing phenates, borated and non-borated sulfonates, borated and non-borated salixarates, borated and non-borated salicylates, and mixtures thereof.

55. The method of claim **36**, wherein the lubricating composition further comprises a "hybrid" detergent formed with mixed surfactant systems comprising a phenate or sulfonate component.

56. The method of claim **36**, wherein the lubricating composition further comprises a phosphorus-containing antiwear agent.

57. The method of claim **36**, wherein the lubricating composition further comprises an ashless succinimide dispersant different from the soot-dispersing additive, wherein the succinimide dispersant is present at 1 wt % to 8 wt %.

58. The method of claim **57**, wherein the succinimide dispersant comprises a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 350 to 5000.

59. The method of claim **57**, wherein the succinimide dispersant comprises a polyisobutylene succinimide, wherein the dispersant has a TBN of at least 40 mg KOH/g and is present in an amount 1.2 wt % to 5 wt % of the lubricating composition.

60. The method of claim **36**, wherein the internal combustion engine has a steel surface on a cylinder bore, cylinder block, or piston ring.

61. The method of claim **36**, wherein the internal combustion engine has a surface of steel, or an aluminum alloy, or an aluminum composite.

62. The method of claim **36**, wherein the oil mist separator is a centrifugal oil mist separator, wherein the centrifugal oil mist separator rotates at 2500 to 10000 rpm.

63. The method of claim **36**, wherein the internal combustion engine has a closed crankcase ventilation.

* * * * *