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(54) DISPERSANT VISCOSITY MODIFIERS WITH SULFONATE FUNCTIONALITY

DISPERGIERMITTELVISKOSITÄTSMODIFIKATOREN MIT SULFONATFUNKTIONALITÄT

MODIFICATEURS DE VISCOSITÉ DISPERSANTS À FONCTIONNALITÉ SULFONATE

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Description

BACKGROUND

[0001] Aspects of the exemplary embodiment relate to a dispersant viscosity modifier, and more specifically to a sulfonated dispersant viscosity modifier and to a lubricating composition, such as an engine oil, which includes the described dispersant viscosity modifier. Aspects of the exemplary embodiment also relate to a method for use of the described dispersant viscosity modifier to improve the film thickness and/or antiwear performance of such a lubricating composition.

[0002] Lubricating oil compositions desirably maintain a relatively stable viscosity over a wide range of temperatures. Viscosity modifiers are often used to reduce the extent of the decrease in viscosity as the temperature is raised or to reduce the extent of the increase in viscosity as the temperature is lowered, or both. Thus, a viscosity modifier ameliorates the change of viscosity of an oil containing it with changes in temperature. The fluidity characteristics of the oil are thereby improved.

[0003] Traditional dispersant viscosity modifiers (DVMs) made from ethylenepropylene copolymers that have been grafted with maleic anhydride and reacted with various amines have shown desirable performance to prevent oil thickening in diesel engines and sludge formation in gasoline engines. However, these materials tend to provide poor antiwear protection, which is an useful performance feature of engine lubricants.

[0004] There is an ongoing need for a viscosity modifier that can provide viscosity and/or sludge control but which also provide good wear protection.

REFERENCES

[0005] U.S. Pat. No. 3,642,728, issued February 15, 1972, entitled SULFONATE POLYMERS, by Canter, discloses sulfonated polymers, such as polymers with low unsaturation formed by the polymerization of ethylene or propylene, particularly polymers with 0.2-10 mole % remaining unsaturation. Sulfonation can be carried out at an aromatic ring within the backbone or pendent therefrom.

[0006] U.S. Pat. No. 3,870,841, issued March 11, 1975, entitled FLEXIBLE POLYMERIC COMPOSITIONS COMPRISING A NORMALLY PLASTIC POLYMER SULFONATED TO ABOUT 0.2 TO ABOUT 10 MOLE % SULFONATE, by Makowski, et al., describes flexible polymeric compositions prepared from sulfonated thermoplastic ionomers by incorporating a plasticizer in the ionomer.

[0007] U.S. Pub. No. 20090305923, published December 10, 2009, entitled DISPERSANT VISCOSITY MODIFIERS BASED ON MALEIC ANHYDRIDE-STYRENE COPOLYMERS, by Visger, et al., discloses dispersant viscosity modifiers based on maleic anhydride-styrene copolymers.

[0008] U.S. Pub. No. 20130303418, published November 14, 2013, entitled HIGH MOLECULAR WEIGHT POLYMERS AS VISCOSITY MODIFIERS, by FALENDER, et al., discloses a lubricating composition which comprises a base oil and between 10 ppm and 1000 ppm by mass of a viscosity modifier, the viscosity modifier comprising an olefin copolymer. The use of additional monomers is anticipated to allow the inventive polymer to have the properties of dispersants, antioxidants, pour point depressants and other additive chemistry.

[0009] U.S. Pub. Nos. 20120178656 and 20120178659, entitled DISPERSANT VISCOSITY MODIFIERS, by Sutton, et al., and Price, et al., disclose a grafted polymer useful as a dispersant viscosity modifier in lubricating compositions. The polymer backbone includes an olefin block and a vinyl aromatic block. The polymer is grafted with a pendant carbonyl containing group, which may be substituted to provide ester, imide and/or amide functionality.

[0010] U.S. Pub. No. 20060173135 by Devlin, et al. describes a lubricating oil composition containing a neutral C_{14}-C_{24} alphaolefin calcium sulfonate.

[0011] U.S. Pat. No. 3,749,695 by de Vries discloses a lubricating oil additive derived from polyisobutylene ethylene diamine with propane sultone.

[0012] U.S. Pat. No. 4,144,181 by Elliot, et al., (claim 2, Examples 5-8) discloses a C_3 to C_{70} hydrocarbyl-substituted sulfonic acid salt of a morpholine derivative of a maleic anhydride graft of an ethylene-propylene copolymer as a dispersant viscosity improver.

[0013] GB 1,121,641 to Castrol Ltd. describes preparation of an additive for a lubricating composition from hydroxy tetraethylene tetramine, polyisobutenyl succinic anhydride and propane sultone.

BRIEF DESCRIPTION

[0014] The invention is defined by and in the appended claims.

[0015] In accordance with one aspect of the exemplary embodiment, a lubricating composition includes an oil of lubricating viscosity and at least 0.05 wt. % of an oil-soluble dispersant viscosity modifier which includes an olefin-based

polymer backbone and at least one pendent functional group selected from alkyl and aryl sulfonate salts, alkyl and aryl sulfonic acids, and combinations thereof, the olefin-based polymer backbone comprising an ethylene-olefin-based co-polymer. Each of the at least one pendent functional group is independently attached to the olefin-based polymer backbone by a linking group. The at least one pendent functional group includes a sulfonate moiety.

[0016] In accordance with another aspect of the exemplary embodiment, a process for making a lubricating composition includes: (i) providing an olefin-based polymer backbone with one or more acylating linking groups, each independently attached along the polymer backbone; (ii) optionally, reacting each acylating group with a hydroxy alkyl amine, an alkylene polyamine, a polyol, or a combination thereof, resulting in an olefin-based polymer with one or more linker units each independently attached along the polymer backbone; and (iii) reacting each linking group or linker unit with a hydrocarbyl sulfonate compound selected from sulfonate salts and sulfonic acids, resulting in a dispersant viscosity modifier comprising one or more pendent hydrocarbyl sulfonate groups each independently attached to the olefin-based polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

FIGURE 1 is a Stribeck plot of traction coefficient vs log mean speed (mm/s) for lubricating compositions formed with and without a sulfonated dispersion viscosity modifier; and

FIGURE 2 is a plot of Central Film Thickness (nm) vs speed (m/s) for lubricating compositions formed with and without a sulfonated dispersion viscosity modifier.

DETAILED DESCRIPTION

[0018] The exemplary embodiment relates to a lubricating composition which includes an oil of lubricating viscosity and a sulfonated dispersant viscosity modifier that includes an olefin-based polymer with pendent groups having sulfonate functionality.

[0019] The exemplary sulfonated dispersant viscosity modifier has improved performance in engine tests, providing a good viscosity index, good soot dispersion and/or toleration properties, while also providing good antiwear protection and/or film thickness performance.

[0020] The exemplary lubricating composition finds particular application as an engine oil for passenger vehicles and heavy duty diesel vehicles.

[0021] The amounts of additives present in the lubricating composition disclosed herein are expressed on an oil free basis, i.e., amount of actives, unless otherwise noted.

The Dispersant Viscosity Modifier

[0022] The exemplary sulfonated dispersant viscosity modifier is a material that provides viscosity modifier performance in a lubricating composition while also providing dispersant functionality. The dispersant viscosity modifier may provide additional and or other benefits to a lubricating composition.

[0023] The exemplary dispersant viscosity modifier is an oil-soluble polymer, which includes a polymer backbone, such as an olefin-based polymer, and one or more pendent hydrocarbyl sulfonate groups each independently attached to the olefin-based polymer. The pendent hydrocarbyl sulfonate groups each include a sulfonate moiety, which can be in the form of a sulfonate salt or a sulfonic acid group, and a hydrocarbyl group, such as an alkyl and/or aryl group, which spaces the sulfonate moiety from the polymer backbone and connects it thereto

[0024] By "oil soluble," it is meant that the dispersion viscosity modifier is soluble in oil at least to the amounts described herein for desirable for serving its intended purpose.

[0025] Each of the pendent groups is attached to the polymer chain by a linking group that is grafted onto the olefin-based polymer or forms a part of the polymer backbone. The linking group thus links the pendent group to the olefin-based polymer. Each linking group may be derived from a dicarboxylic acid, such as maleic anhydride, that can be linked to the pendent group directly or indirectly, via a linker unit. In the case of a linker unit, the linking group may be grafted to the polymer backbone by first reacting a dicarboxylic acid, such as maleic anhydride, to the polymer backbone using a peroxide catalyst to form the linking group and then attaching the linker unit by esterification, imidation or amidation.

[0026] The sulfonated dispersant viscosity modifier can be represented by a molecule of the general formula (I):

$$P\text{-}(X\text{-}Y\text{-}Z)_x \qquad (I),$$

where P represents the olefin-based polymer, X represents the linking group, Y represents an optional intermediate

linker unit, Z represents the pendent hydrocarbyl sulfonate group, and x is at least 1, such as from 1 to 20, or 1 to 10, or 1 to 8, e.g., at least 2. As it will be appreciated, there may be many molecules of Formula (I) in the lubricating composition, so the values of x may be considered number average values over all the molecules present. A ratio by weight of linking groups X to the polymer backbone P in the dispersant viscosity modifier may be at least 1:100, or at least 2:100, such as at least 3:100, and in some embodiments, is up to up to 20:100 or up to 10:100. As will be appreciated, P in Formula (I) may contain a range of molecular weights, commonly characterized by a molecular weight distribution, so the values of x may be considered number average values over all the molecules present.

[0027] In some embodiments, P is an ethylene-olefin-based copolymer and the viscosity modifier of Formula (I) is represented by Formula (II) or (III):

$$-[[(CH_2)_m\text{-}(CHR^1\text{-}CH_2)_n)]_{p\text{-}q}\text{-}[(CH_2)_m\text{-}(CR^1(X\text{-}Y\text{-}Z)\text{-}CH_2)_n]_q]_k\text{-} \quad \text{(II)}$$

$$-[[(CH_2)_m\text{-}(CHR^1\text{-}CH_2)_n]_p\text{-}[X(Y\text{-}Z)]_q]_k\text{-} \quad \text{(III)}$$

where each R^1 represents H or an alkyl group containing from 1 to 8 carbon atoms,

m, n, p and q are independently at least 1,
k is at least 1, such as at least 2.

[0028] In some embodiments, a ratio of m:n may be from 1 to 6. The ratio of m:n may be 1.5 to 2.3, or 2.3 to 3.5, or 3.5 to 6. In some embodiments, a ratio of the number of hydrocarbyl sulfonate groups q : number ethylene olefin units p in the molecules of Formulas (II) and (III) (e.g., averaged over all molecules) is at least 0.01. In some embodiments, the ratio of q:p may be at least 0.02, or at least 0.03, or at least 0.1, or at least 0.2 and may be up to 0.9, or up to 0.5.

[0029] Formula (II) represents a viscosity modifier in which the linking group X is grafted onto the polymer backbone P, which can be of the general form $-[(CH_2)_m\text{-}(CHR^1\text{-}CH_2)_n]_p-$ prior to grafting. Formula (III) represents a viscosity modifier in which the linking group X is integral with the polymer backbone P.

[0030] As will be appreciated, fewer than all of the linking groups X may be linked to a hydrocarbyl sulfonate group Z, although in one embodiment, a majority (at least 50%), or substantially all (at least 80%, or at least 90%, or at least 95%), or all of the linking groups X are linked to a respective hydrocarbyl sulfonate group Z.

[0031] The hydrocarbyl sulfonate group Z may be derived from a hydrocarbyl sulfonate compound, such as an alkyl or aryl sulfonic acid, source thereof, or salt thereof. The hydrocarbyl sulfonate group Z can be represented by the general formula $-[R^2(SO_3)^-]_rM^{r+}$, where R^2 represents a hydrocarbyl group, and M^{r+} represents a cation, where r is at least 1. The sulfonate moiety in the hydrocarbyl sulfonate group Z can thus be represented by $-[(SO_3)^-]_rM^{r+}$. M^{r+} may be selected from H^+ (the acid form) and other cations, such as metal cations and aliphatic amine cations of the form $-(NR^3R^4R^5)$, where R^3, R^4, and R^5 are independently selected from H and C_1 to C_{30} hydrocarbyl groups, such as aliphatic groups, e.g., C_1 to C_{30} alkyl groups. In one embodiment, at least one or at least two of R^3, R^4, and R^5 is an alkyl group and in another embodiment, each of R^3, R^4, and R^5 is an alkyl group. In some embodiments, the alkyl groups have at least 2, or at least 3, or up to 20, or up to 10 carbon atoms. Example metal cations include alkali metals, such as K^+, Na^+, Mg^{+2}, Ca^{2+}, and mixture thereof. In some embodiments, the dispersant viscosity modifier is metal free, and the cation is a non-metal cation. To avoid crosslinking, the cation is suitably a monovalent cation, i.e., r is 1, although minor amounts of multivalent cations may be present. Where a base is to be present in the lubricating composition, the sulfonate moiety may be selected from oil-soluble salts to avoid formation of oil-insoluble or sparingly soluble salts through reaction with the base.

[0032] The term "hydrocarbyl group" is used herein 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:

(i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
(ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
(iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms.

[0033] Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, and in some embodiments, no more than one non-hydrocarbon substituent is

present for every ten carbon atoms in the hydrocarbyl group. In one embodiment, there are no non-hydrocarbon substituents in the hydrocarbyl group.

[0034] In one embodiment, the hydrocarbyl group R^2 of the hydrocarbyl sulfonate group Z is or includes an alkyl group, such as a C_3 to C_{24} alkyl group or C_3-C_{20} alkyl group, which spaces the sulfonate moiety from the polymer backbone by at least three carbon atoms, which may be in the form of a chain and/or ring. In another embodiment, the hydrocarbyl group R^2 is or includes an aryl group, such as a C_6 to C_{20} aryl group which spaces the sulfonate moiety from the polymer backbone by an aromatic ring. One or more of the carbons in the hydrocarbyl group R^2 may be substituted with heteroatoms.

[0035] In some embodiments, the sulfonated dispersant viscosity modifier includes from 1 to 50 of the described hydrocarbyl sulfonate groups Z, or from 1 to 30, or from 1 to 20, or 1 to 10, or from 1 to 6, or 1 to 4, per molecule of the dispersant viscosity modifier, on average. In some embodiments, the sulfonated dispersant viscosity modifier includes 1, 2, 3, 4, 5 or 6 hydrocarbyl sulfonate groups Z, on average.

[0036] The exemplary linking groups X are acylating groups, each independently attached along the polymer's backbone. The linking group X may be derived from an ethylenically unsaturated carboxylic acid monomer, such as a dicarboxylic acid, or functional equivalent thereof, or a polyol. In one embodiment, the intermediate linker unit Y may be derived from a hydroxy alkyl amine, an alkylene polyamine, or a combination thereof. In some embodiments, the linking group X is derived from maleic anhydride and the linker unit Y is derived from a hydroxy alkyl amine. In some embodiments, the unsaturated carboxylic reactant is grafted on to the olefin-based polymer backbone and the hydroxy alkyl amine and/or alkylene polyamine is reacted with the unsaturated carboxylic reactant group containing olefin-based polymer backbone. In other embodiments, the unsaturated carboxylic reactant is present in the olefin-based polymer backbone and the hydroxy alkyl amine and/or alkylene polyamine is reacted with the unsaturated carboxylic reactant group containing olefin-based polymer backbone.

[0037] In another embodiment, the hydrocarbyl sulfonate compound includes an amine or -OH functional group which can serve as an intermediate linker unit Y. In this embodiment, the unsaturated carboxylic reactant may be grafted on to the olefin-based polymer backbone and the amine/alcohol functional group of the hydrocarbyl sulfonate compound is reacted with the unsaturated carboxylic reactant group containing olefin-based polymer backbone. Where the unsaturated carboxylic reactant is present in the olefin-based polymer backbone the amine/alcohol functional group of the hydrocarbyl sulfonate compound is reacted with the unsaturated carboxylic reactant group containing olefin-based polymer backbone.

[0038] The polymer backbone P employed in the sulfonated dispersant viscosity modifier is not particularly limited, provided that it can be modified with a carboxylic acid functionality or a reactive equivalent of the carboxylic acid functionality (e.g., anhydride or ester) that serves as the linking group described above.

[0039] Suitable olefin-based polymer backbones P include ethylene, propylene, and butylene polymers, copolymers thereof, copolymers thereof further containing a non-conjugated diene, and isobutylene/conjugated diene copolymers, each of which can be subsequently supplied with, e.g. grafted with, carboxylic functionality to serve as the linking group or have carboxylic functionality in the backbone itself (such as an ethylene-co-propylene-co-maleimide copolymer). In some embodiments, the polymer backbone P is a copolymer of ethylene and an α-olefin, such as propylene and/or butylene. Example ethylene-olefin-based polymers include ethylene propylene copolymers. In some embodiments, the olefin-based polymer is a copolymer where ethylene makes up at least 10 % of the monomer used to prepare the copolymer on a molar basis, or at least 20 mole %, or at least 50 mole %.

[0040] Ethylene-propylene or higher alpha monoolefin copolymers may consist of 15 to 80 mole % ethylene and 20 to 85 mole % propylene or higher monoolefin. In some embodiments, the mole ratio is 30 to 80 mole % ethylene and 20 to 70 mole % of at least one C_3 to C_{10} alpha monoolefin, for example, 50 to 80 mole % ethylene and 20 to 50 mole % propylene. Terpolymer variations of the foregoing polymers may contain up to 15 mole %, or up to 10 mole % of a non-conjugated diene or triene.

[0041] In these embodiments, the polymer backbone (e.g., the ethylene copolymer or terpolymer), can be an oil-soluble, substantially linear, rubbery material. Also, in certain embodiments, the polymer can be in forms other than substantially linear, that is, it can be a branched polymer or a star polymer. The polymer can also be a random copolymer or a block copolymer, including di-blocks and higher blocks, including tapered blocks and a variety of other structures.

[0042] The polymer backbone (olefin-based polymer) may have a number average molecular weight Mn (measured by gel permeation chromatography, using a polystyrene standard), which can be up to 150,000 or higher, e.g., at least 1,000 or at least 3,000 or at least 5,000, such as up to 150,000 or up to 120,000, or up to 100,000, or up to 50,000, or up to 15,000, e.g., about 3,000 to about 15,000. The sulfonated dispersant viscosity modifier may have a number average molecular weight Mn (by gel permeation chromatography, polystyrene standard), which can be up to 150,000 or higher, e.g., at least 2,000 or at least 3,000 or at least 5,000, such as up to 150,000 or up to 120,000, or up to 100,000, or up to 50,000, or up to 18,000, e.g., about 4,000 to about 16,000.

[0043] The term "polymer" is used generically to encompass homopolymers, i.e., polymers of a single monomer, as well as copolymers, terpolymers and/or interpolymers. These materials may contain minor amounts of other olefinic

monomers so long as their basic characteristics are not materially changed.

[0044] In one embodiment, the exemplary sulfonated dispersant viscosity modifier is formed by reacting a carboxylic acid-modified polymer backbone with a hydroxy alkyl amine and/or alkylene polyamine and/or polyol and a hydrocarbyl sulfonate compound. In another embodiment, the exemplary dispersant viscosity modifier may be formed by reacting a carboxylic acid-modified polymer backbone with an amino-substituted hydrocarbyl sulfonate compound. Where a sulfonic acid is formed, the acid may be converted to its salt through reaction with a suitable base.

[0045] The unsaturated carboxylic acid monomer used to form the linking group X may be derived from maleic acid and/or anhydride. As noted above, this portion of the linking group may be incorporated and/or attached to the polymer backbone during the polymerization of the polymer backbone, for example, by mixing a monomer containing the linking group in with the other monomers used to prepare the polymer backbone. In other embodiments, this part of the linking group may be added by grafting the group onto an already prepared polymer backbone.

[0046] As noted above, in some embodiments the unsaturated carboxylic acid used to form the linking group is contained within a monomer copolymerized within the polymer backbone chain. In other embodiments, the unsaturated carboxylic reactant may be present as a pendent group attached by, for example, a grafting process.

[0047] Examples of suitable carboxylic-acid containing polymers, which are representative of the polymer backbone described above with carboxylic reactant portion of the liking group attached, include maleic anhydride-ethylene-propylene copolymers, maleic anhydride-styrene copolymers, including partially esterified versions thereof, and copolymers thereof. Nitrogen-containing esterified carboxyl-containing interpolymers prepared from maleic anhydride and styrene-containing polymers are described in U.S. Pat. No. 6,544,935 to Vargo et al. Other polymer backbones which are used for preparing dispersants may also be used. For example, polymers derived from isobutylene and isoprene are described in U.S. Pub. No. 20040034175 to Kolp. Other suitable polymer backbones include substantially hydrogenated copolymers of vinyl aromatic materials such as styrene and unsaturated hydrocarbons such as conjugated dienes, e.g., butadiene or isoprene. In substantially hydrogenated polymers of this type, the olefinic unsaturation is typically substantially completely hydrogenated by known methods, but the aromatic unsaturation may remain. Such polymers can include random copolymers, block copolymers, or star copolymers. Yet other suitable backbone polymers include styrene-ethylene-alpha olefin polymers, as described in PCT publication WO 2001/030947, and polyacrylates or polymethacrylates, generically called poly(meth)acrylates. In the case of such poly(meth)acrylates, the (meth)acrylate monomers within the polymer chain itself may serve as the carboxylic acid functionality or reactive equivalent thereof which is used to react with the amine functionality which provides the linker unit Y. Alternatively, additional acid functionality may be copolymerized into the (meth)acrylate chain or even grafted onto it, particularly in the case of acrylate polymers.

[0048] In certain embodiments, the polymer backbone may be prepared from ethylene and propylene or it may be prepared from ethylene and a higher olefin within the range of (C_3 to C_{10}) alpha-monoolefins, which may then in either case be grafted with a suitable carboxylic acid-containing monomer, to serve as the linking group X.

[0049] More complex polymer backbones, often designated as interpolymers, may also be included. Such materials are generally used to prepare an interpolymer backbone is a polyene monomer selected from conjugated or non-conjugated dienes and trienes. The non-conjugated diene component is one having from about 5 to about 14 carbon atoms. In one embodiment, the diene monomer is characterized by the presence of a vinyl group in its structure and can include cyclic and bicyclo compounds. Representative dienes include 1,4-hexadiene, 1,4-cyclohexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 1,5-heptadiene, and 1,6-octadiene. A mixture of more than one diene can be used in the preparation of the interpolymer.

[0050] The ethylenically unsaturated carboxylic acid monomer may be grafted onto the polymer backbone in a number of ways, such that a resulting polymer intermediate with linking groups X is characterized by having carboxylic acid acylating functions within its structure. Such materials which are attached to the polymer typically contain at least one ethylenic bond (prior to reaction) and at least one, or at least two, carboxylic acid (or its anhydride) groups or a polar group which is convertible into the carboxyl groups by oxidation or hydrolysis. Maleic anhydride or an alkyl-substituted derivative thereof (e.g., methyl maleic anhydride or ethyl maleic anhydride) is suitable for forming the linking groups. It grafts onto the ethylene copolymer or terpolymer to give two carboxylic acid functionalities. Examples of additional unsaturated carboxylic materials include chlormaleic anhydride, itaconic anhydride, and the corresponding dicarboxylic acids, such as maleic acid, fumaric acid, acrylic acid, cinnamic acid, and their esters.

[0051] Example intermediate polymers of this type are available from Mitsui under the tradename Lucant™, such as Lucant™A-5320H polymer. Lucant A-5320H is an amorphous copolymer of ethylene and propylene (GPC M_n=7700) that is randomly grafted with maleic anhydride (in the presence of a free radical peroxide initiator in a high shear mixer) to a level of about 3.5 weight % maleic anhydride. The final product has molecular weight (GPC polystyrene standards) M_n=8810 and M_w=17200 and a Total Acid Number of 40 to 45 mg KOH/g.

[0052] The polymer intermediate may then be reacted with the hydroxy alkyl amine, alkylene polyamine, or polyol to provide the intermediate polymer with linker units Y. In other embodiments, the polymer intermediate is reacted directly with an amine-substituted hydrocarbyl sulfonate compound or other substituted hydrocarbyl sulfonate compound capable of reaction with the intermediate polymer.

[0053] Hydroxy alkyl amines and/or alkylene polyamines suitable for forming linker units Y are not overly limited. In some embodiments, they may be represented by the general formula:

$$R^6R^7N\text{-}R^8\text{-}OH$$

or

$$R^6R^7N\text{-}R^8\text{-}NR^6R^7$$

where each R^6 and R^7 is independently hydrogen or a hydrocarbyl group containing from 1 to 6 carbon atoms and each R^8 is independently an alkylene group containing from 1 to 10 carbon atoms.

[0054] Suitable hydroxy alkyl amines include amines having at least one amine group and at least one hydroxyl group, where the amine group is a primary, secondary, or tertiary amine group. The hydroxy alkyl amines may have 2 to 30 carbon atoms. Example hydroxy alkyl amines may include mono-, di- and tri-alkoxylates of ammonia such as mono- and di- and tri-ethanolamine, hydroxy-containing monoamines such as a diethoxylated C_{16} to C_{18} tallowamine, and hydroxy-containing polyamines such as 2-(2-aminoethylamino)ethanol. In some embodiments the hydroxy alkyl amine includes 3-hydroxypropyl amine.

[0055] Suitable polyamines for forming linker units Y may have from 2 to 30 carbon atoms. Example polyamines include alkylenediamines, N-alkyl alkylenediamines, and polyalkylenepolyamines. Useful polyamines include ethylenediamine, 1,2-diaminopropane, N-methylethylenediamine, N-tallow(C_{16}-C_{18})-1,3-propylenediamine, N-oleyl-1,3-propylenediamine, polyethylenepolyamines such as diethylenetriamine and triethylenetetramine and tetraethylenepentamine and polyethylenepolyamine bottoms.

[0056] Suitable polyols for forming linker units Y are not overly limited. In some embodiments, they may be represented by the general formula:

$$HO\text{-}R^9\text{-}OH$$

where R^9 is hydrocarbyl group, and in some embodiments an alkylene group, containing from 1 to 10 carbon atoms. In some embodiments, the sulfonated dispersant viscosity modifier is prepared using an alkylene diol, an amino-polyol, or combinations thereof. Examples of suitable diols include butanediol, hexanediol, 2-amino-2-hydroxymethyl-propane-1,3-diol, and combinations thereof.

[0057] As noted above, the reaction product of the olefin-based polymer backbone containing the unsaturated carboxylic reactant and the hydroxy alkyl amine and/or alkylene polyamine and/or polyol may then be reacted with the hydrocarbyl sulfonate compound to provide the dispersant viscosity modifier.

[0058] In some embodiments, the sulfonated dispersant viscosity modifier is the reaction product of (i) an olefin-based polymer, for example an ethylene propylene copolymer, that has been functionalized with a unsaturated carboxylic reactant, for example, by using maleic anhydride, and (ii) a hydroxy alkyl amine and/or an alkylene polyamine, for example, a hydroxy alkyl amine such as 3-hydroxypropylamine. The resulting intermediate can then be reacted with a hydrocarbyl sulfonate compound (which may thereafter be converted to a salt) to provide a dispersant viscosity modifier.

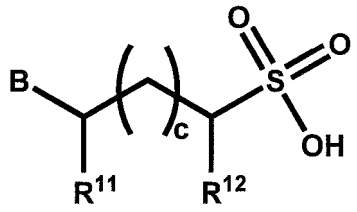
[0059] In other embodiments, the sulfonated dispersant viscosity modifier is the reaction product of (i) an olefin-based polymer, for example an ethylene propylene copolymer, that has been functionalized with a unsaturated carboxylic reactant, for example, by using maleic anhydride, and (ii) an amine-substituted hydrocarbyl sulfonate compound (which may thereafter be converted to a salt by reaction with a base) to provide a dispersant viscosity modifier.

[0060] Suitable hydrocarbyl sulfonate compounds for forming the pendent functional groups are of the general form:

$$B\text{-}A\text{-}SO_3M$$

where A represents a hydrocarbyl group or a substituted hydrocarbyl group, M is a cation as described above, and B represents a functional group capable of reacting with the linker unit Y, or capable of undergoing direct acylation with the linking group X. B can be NH_2 (giving an amine-substituted hydrocarbyl sulfonate compound, $H_2N\text{-}A\text{-}SO_3M$) or OH. The hydrocarbyl sulfonate compounds can also be in the form of a ring capable of reaction with water to form $B\text{-}A\text{-}SO_3H$. The hydrocarbyl group A may be at least 3 carbons in length and may be selected from C_3-C_{20} alkyl groups and C_6-C_{24} aryl or alkylaryl groups, as discussed for R^2 above. M may represent a monovalent cation. Where group B is capable of acylation by the linking group, the linker unit can be omitted, although it may still be useful for chain extension to space the lipophilic sulfonate moiety further from the backbone.

[0061] Example alkyl hydrocarbyl sulfonate compounds suitable for forming the pendent functional groups include aliphatic sulfonic acids represented by formula (IV):

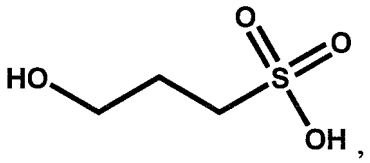


(IV),

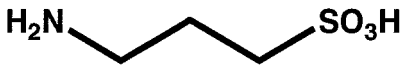
where c is from 1-10,

B is NH_2 or OH, and
R^{11} and R^{12} are independently H or a C_1 to C_{30} alkyl group.

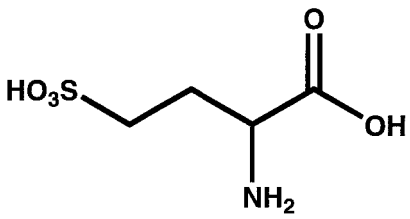
[0062] Examples of formula (V) include 3-hydroxypropane-1-sulfonic acid:



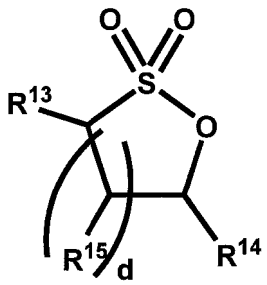
and 3-amino-1-propane sulfonic acid:



[0063] Examples of substituted alkyl sulfonate compounds include homocysteic acid:



[0064] Example cyclic sulfonic acids, known as sultones which have the sulfonyl-oxy group $-OSO_2-$ in a ring, can be represented by formula (V):

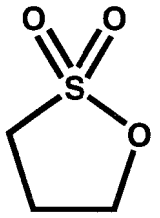


(V)

where d is from 1-10, such as 1 or 2, and

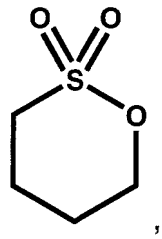
R^{13}, R^{14}, and R^{15} are independently H or a C_1 to C_{30} alkyl group.

[0065] Useful sultones include, for example, 1,3-propanesultone (d = 1, R^{13}, R^{14}, R^{15} = H),



,

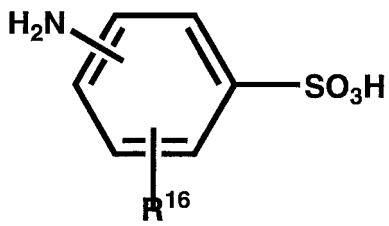
1,4-butanesultone (d = 2, R^{13}, R^{14}, R^{15} = H):



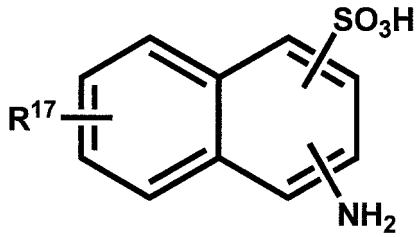
,

and C_1-C_{10} alkyl-substituted derivatives thereof, such as those with CH_3 substitutions at one or more of the R^{13}, R^{14}, and R^{15} positions. Sultones can react in water to form the corresponding hydroxyalkyl sulfonic acid. Such hydrocarbyl sulfonate compounds are capable of reaction with OH groups of the linker units Y of the intermediate polymer. For example, 1,3-propanesultone yields products with a terminal -CH_2-CH_2-CH_2-SO_3H group and 1,4-butanesultone yields products with a terminal -CH_2-CH_2-CH_2-CH_2-SO_3H group, where the terminal H can subsequently be converted to another cation M as described above.

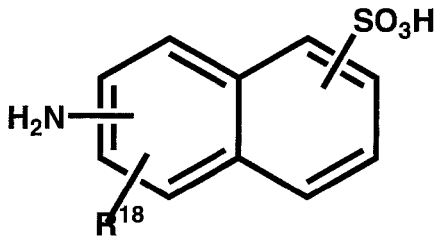
[0066] Examples of aryl sulfonate compounds include those of general formulas (VI), (VII), (VIII), (IX), and (X):



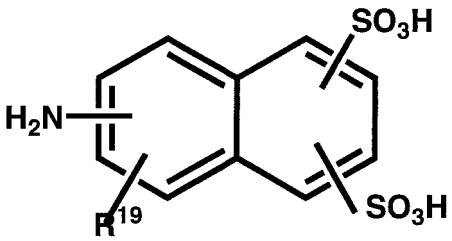
(VI),



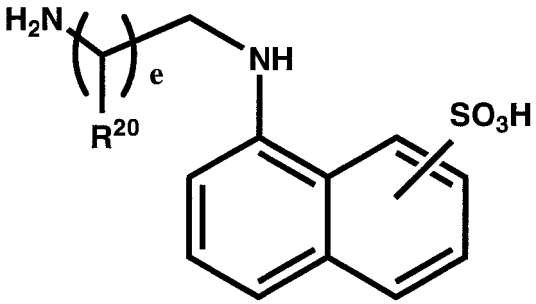
(VII),



(VIII),



(IX),



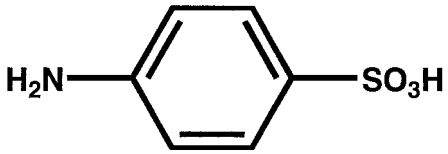
(X),

where R^{16}, R^{17}, R^{18}, and R^{19}, are independently selected from H, OH, NH_2, C_1-C_{30} (or C_1-C_{10}) alkyl groups, and alkoxy groups,

R^{20} is H or a C_1-C_{30} (or C_1-C_{10}) alkyl group, and
e is at least 1, such as 1-20 or 1-10,

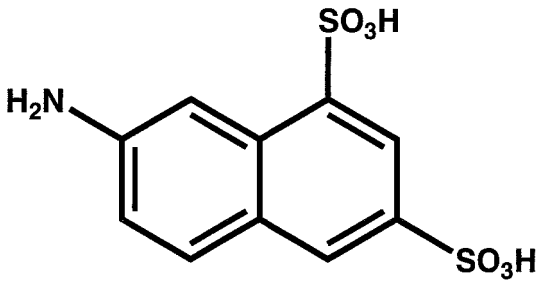
[0067] In exemplary embodiments, the NH_2 group may be positioned *ortho*, *meta*, or *para* to the sulfonic acid group. Additional substituents, e.g., just one, can be positioned on the ring in the locations not occupied by the amine or sulfonic acid. In some embodiments the substituent is a methyl group, but can also be a hydroxy (-OH) group, an alkoxy (-OR) group, a nitroxy (-NO_2) group, or another amine.

[0068] Examples of aryl sulfonate compounds according to formula (VI) include *p*-aminobenzenesulfonic acid (sulfanilic acid):

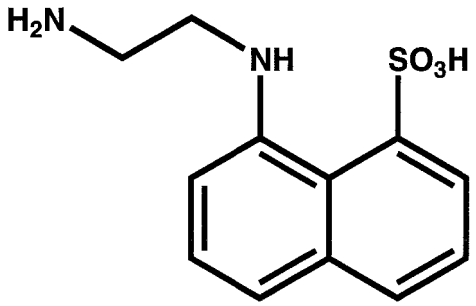


[0069] As illustrated in Formulas (VII), (VIII), (IX), and (X) the aryl group can be based on naphthalene. In such embodiments, the sulfonic acid may occupy either the 1 or 2 position on the ring and the amine may be either on the same ring or on the adjoining ring. Substituents can be the same noted for single ring aryl groups and may occupy any sites not occupied by the amine or sulfonic acid.

[0070] Examples of aryl sulfonate compounds according to formula (IX) include 7-amino-1,3-naphthene disulfonic acid:



[0071] Examples of aryl sulfonate compounds according to formula (X) include 8-(2-aminoethylamino)-1-naphthene sulfonic acid:



and substituted derivatives thereof.

[0072] Where the resulting molecule includes a sulfonate moiety which is a sulfonic acid, it can be subsequently converted to the salt by reaction with a suitable base. Exemplary bases for conversion of the acid form of the sulfonate moiety to the respective sulfonate salt include metal hydroxides, such as NaOH, KOH, and $Ca(OH)_2$, and alkyl amines, such as di- or tri-alkyl amines of the general form $NR^3R^4R^5$, where R^3, R^4, and R^5 are as described above. The alkyl amine may have alkyl groups having 1 to 30, or 2 to 20, or 3 to 10 carbon atoms. Examples of dialkyl amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, di-(2-ethylhexyl)amine, di-decylamine, di-dodecylamine, di-stearylamine, di-oleylamine, di-eicosylamine, and mixtures thereof. Examples of trialkyl amines include trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, tri-(2-ethylhexyl)amine, tri-decylamine, tridodecylamine, tri-stearylamine, tri-oleylamine, tri-eicosylamine, and mixtures thereof.

[0073] The reaction can be carried out in a suitable solvent, such as a diluent oil and/or toluene, at a sufficient temperature, such as at least 90°C or at least 100°C, but below the boiling point of the solvent or the decomposition temperature of the product. Alternately, the reaction can be accomplished in the substantial absence of solvent, e.g., in a twin screw extruder, Banbury mixer, or similar device.

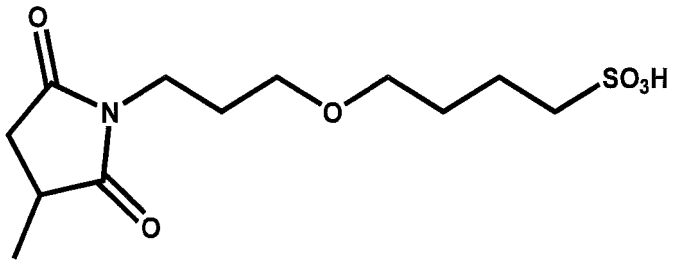
[0074] The sulfonated dispersant viscosity modifier may be present in the lubricating composition at a concentration of at least 0.05 weight %, such as at least 0.1 weight %, or at least 0.2 weight %, or at least 0.5 weight %. The sulfonated dispersant viscosity modifier may be present in the lubricating composition at a concentration of up to 10 weight %, such as up to 5 weight %, or up to 3 weight %, or up to 2.3 weight %.

[0075] HLB values reported herein are determined by the Griffin Method (see Griffin, William C. (1949), "Classification of Surface-Active Agents by 'HLB'", Journal of the Society of Cosmetic Chemists 1 (5): 311-26 and Griffin, William C. (1954), "Calculation of HLB Values of Non-Ionic Surfactants", Journal of the Society of Cosmetic Chemists 5 (4): 249-56

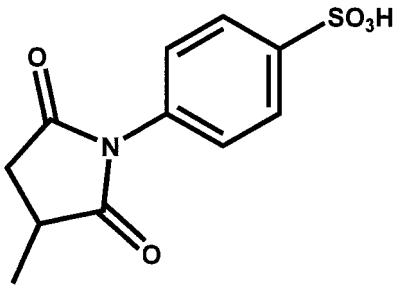
[0076] In Griffin's method, HLB = 20*M*h*/M, where M*h* is the molecular mass of the hydrophilic portion of the molecule and M is the molecular mass of the whole molecule. This method covers a range from 0-20.

[0077] The exemplary sulfonated dispersant viscosity modifier may have an HLB value according to the Griffin method, of 1-10, or at least 2, or at least 2.5, or at least 3, and can be up to 9 or up to 8, or up to 7.

[0078] For example, a sulfonated dispersant viscosity modifier with an ethylene propylene backbone having about 240 CH_2/CH/CH_3 groups has an molecular mass of approximately 3525, as determined by vapor phase osmometry (VPO). When reacted with 3.5 wt % maleic anhydride (e.g., forming Lucant A-5320H), each polymer backbone chain has, on average, 3.5 sites which can be functionalized with the sulfonate moiety. When reacted with 3-aminopropanol (as a linker unit), and sulfanilic acid or butane sultone this provides a head group of the form:



(molecular weight 292.3), or



(molecular weight 254.2)

[0079] Considering these entire head group portions as the respective hydrophilic portion, the Mh term is approximately 292.3*3.5=1023 for the alkyl sulfonic acid-based head group. Therefore, the HLB = 20*1023/(3525+1023) = 4.5 for a dispersant viscosity modifier composed of an ethylenepropylene copolymer with alkyl sulfonic acid pendent groups.

[0080] In a similar fashion, the HLB for the dispersant viscosity modifier composed of an ethylenepropylene copolymer with aryl sulfonic acid pendent groups can be computed as 4.0.

[0081] For polymer backbones prepared with greater amounts of maleic anhydride grafted onto them, such as 6.2 groups per chain, the HLB range can be up to about 6.8 or higher for the alkyl sulfonic acid and up to about 6.2 for the aryl sulfonic acid dispersion viscosity modifiers.

[0082] Under the method described herein, the entire head group is considered as the hydrophilic portion, even though it contains some hydrocarbon portions.

Oils of Lubricating Viscosity

[0083] The exemplary lubricating composition includes an oil of lubricating viscosity. Suitable oils include both natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof.

[0084] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0085] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0086] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0087] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[0088] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as poly α-olefins, and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetra-decylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0089] Other synthetic lubricating oils include polyol esters (such as Priolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be 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.

[0090] The base oil may be selected from any of the base oils in Groups I-V of the American Petroleum Institute (API) Base Oil Interchangeability Guidelines, namely

Base Oil Category	Sulfur (%)	Saturates(%)	Viscosity Index
Group I	>0.03 and/or	<90	80 to 120
Group II	≤0.03 and	≥90	80 to 120
Group III	≤0.03 and	≥90	>120
Group IV	'All polyalphaolefins (PAOs)		
Group V	All others not included in Groups I, II, III or IV		

[0091] Groups I, II and III are mineral oil base stocks. 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". In one embodiment, the oil of lubricating viscosity may be an API Group II or Group III oil. In another embodiment, the oil of lubricating viscosity may be an API Group I oil.

[0092] The oil of lubricating viscosity may have a kinematic viscosity of less than 15 mm^2/s (cSt) at 100 °C, and in other embodiments 1-12 or 2-10 or 3-8 or 4-6 mm^2/s. Kinematic viscosity is determined by ASTM D445-14, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)," ASTM International, West Conshohocken, PA, 2003, DOI: 10.1520/D0445-14. The dispersant viscosity modifier may have a kinematic viscosity at 100 °C of at least 35 mm^2/s, or at least 100 mm^2/s, or at least 500 mm^2/s.

[0093] 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 sulfonated dispersant viscosity modifier and the other performance additives. The oil of lubricating viscosity may be present in the lubricating composition at a concentration of at least 10 wt %, or at least 20 wt %, or at least 40 wt %, or at least 80 wt %, and may be up to 99 wt %, or up to 95 wt %, or up to 90 wt %.

[0094] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition (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. If the lubricating composition (comprising the additives disclosed herein) is in the form of a finished lubricant, the ratio of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99.9 to 50:50 by weight, or 1:99 to 30:70 by weight.

Additional Performance Additives

[0095] The lubricating composition optionally includes one or more additional performance additives. These additional performance additives may include one or more metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants, dispersant viscosity modifiers (other than the exemplary compound), extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, antiwear agents, and any combination or mixture thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives, and often a package of multiple performance additives.

[0096] In one embodiment, the lubricating composition further includes a dispersant, an antiwear agent, a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, or a combination thereof, where each of the additives listed may be a mixture of two or more of that type of additive. In one embodiment, the lubricating composition further includes a polyisobutylene succinimide dispersant, an antiwear agent, a friction modifier, a viscosity modifier (typically an olefin copolymer such as an ethylene-propylene copolymer), an antioxidant (including phenolic and aminic antioxidants), an overbased detergent (including overbased sulfonates and phenates), or a combination thereof, where each of the additives listed may be a mixture of two or more of that type of additive.

[0097] In one embodiment, the lubricating composition further includes an antiwear agent such as a metal dihydrocarbyl dithiophosphate (typically zinc dialkyldithiophosphate), wherein the metal dihydrocarbyl dithiophosphate contributes at least 100 ppm, or at least 200 ppm, or 200 ppm to 1000 ppm, or 300 ppm to 800 ppm, or 400 ppm to 600 ppm of phosphorus to the lubricating composition. In one embodiment, the lubricating composition is free of or substantially free of zinc dialkyldithiophosphate (ZDDP).

[0098] In one embodiment, the lubricating composition further includes a dispersant. The dispersant may be present at a concentration of 0 wt % to 20 wt %, such as at least 0.01 wt %, or at least 0.1 wt %, or at least 0.1 wt %, or at least 1 wt %, or up to 20wt%, or up to 15 wt %, or up to 10 wt %, or up to 6 wt % of the lubricating composition. In one embodiment, the dispersant may be present in the composition at a concentration of 0.2 wt % to 2 wt %.

[0099] Suitable dispersants for use in the exemplary lubricating compositions include succinimide dispersants. 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.

[0100] The succinimide dispersant may be a derivative of an aliphatic polyamine, or mixtures thereof. 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 selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0101] The dispersant may be a N-substituted long chain alkenyl succinimide. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide. Typically, the polyisobutylene from which a 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 example, 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.

[0102] The dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0103] In one embodiment, the lubricating composition further includes a dispersant viscosity modifier other than the sulfonated dispersant viscosity modifier described herein. The additional dispersant viscosity modifier may be present at a concentration of 0 wt % to 5 wt %, such as at least 0.01 wt %, or at least 0.05 wt %, or up to 5 wt %, or up to 4 wt %, or up to 2 wt % of the lubricating composition.

[0104] Suitable dispersant viscosity modifiers include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalized with an amine, and esterified styrene-maleic anhydride copolymers reacted with an amine. Exemplary dispersant viscosity modifiers are disclosed, for example, in WO2006/015130 and U.S. Pat. Nos. 4,863,623; 6,107,257; 6,107,258; and 6,117,825.

[0105] In one embodiment, the lubricating composition further includes a phosphorus-containing antiwear agent. The antiwear agent may be present at a concentration of 0 wt % to 3 wt %, such as at least 0.1 wt %, or at least 0.5 wt %, or up to 3 wt %, or up to 1.5 wt %, or up to 0.9 wt % of the lubricating composition. The phosphorus-containing antiwear agent may be a zinc dialkyldithiophosphate, or mixture thereof.

[0106] In one embodiment, the lubricating composition further includes a molybdenum compound. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof.

[0107] In one embodiment, the lubricating composition further includes an overbased detergent. The overbased detergent may be present at 0 wt % to 15 wt %, or at least 0.1 wt %, or at least 0.2 wt %, or at least 0.2 wt %, or up to 15 wt %, or up to 10 wt %, or up to 8 wt %, or up to 3 wt % of the lubricating composition. For example, in a heavy duty diesel engine, the detergent may be present at 2 wt % to 3 wt % of the lubricating composition. For a passenger car engine, the detergent may be present at 0.2 wt % to 1 wt % of the lubricating composition.

[0108] The overbased detergent may be selected from the group consisting of non-sulfur containing phenates, sulfur containing phenates, sulfonates, salixarates, salicylates, and mixtures thereof.

[0109] The overbased 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 can be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0110] Suitable overbased detergents are sodium salts, calcium salts, magnesium salts, or mixtures of the phenates, sulfur containing phenates, sulfonates, salixarates and salicylates. Overbased phenates and salicylates may have a total base number of 180 to 450 TBN. Overbased sulfonates may have a total base number of 250 to 600, or 300 to 500. In one embodiment, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8, as described, for example, in U.S. Pub. No. 20050065045. The linear alkylbenzene sulfonate

detergent may be particularly useful for assisting in improving fuel economy. The linear alkyl group may be attached to the benzene ring anywhere along the linear chain of the alkyl group, but often in the 2, 3, or 4 position of the linear chain, and in some instances, predominantly in the 2 position, resulting in the linear alkylbenzene sulfonate detergent.

[0111] In one embodiment, the lubricating composition includes an antioxidant, or mixture of antioxidants. The antioxidant may be present at 0 wt % to 15 wt 5, or 0.1 wt % to 10 wt %, or 0.5 wt % to 5 wt % of the lubricating composition.

[0112] Antioxidants include sulfurized olefins, alkylated diarylamines (typically alkylated phenyl naphthyl amines for example those commercially available as Irganox® L 06 from CIBA, or alkylated diphenylamines such as dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine), hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), or mixtures thereof.

[0113] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a steric 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. Patent 6,559,105.

[0114] In one embodiment, the lubricating composition further includes a friction modifier. The friction modifier may be present at 0 wt % to 6 wt %, such as at least 0.05 wt %, or at least 0.1 wt %, or up to 6 wt %, or up to 4 wt %, or up to 2 wt % of the lubricating composition. In one embodiment, the friction modifier is present in the composition at 0.1 to 1.0 wt %. Examples of friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; or fatty alkyl tartramides. In some embodiments, the term fatty, as used herein, can mean having a C_8 to C_{22} linear alkyl group.

[0115] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid.

[0116] In one embodiment, the friction modifier may be selected from the group consisting of long chain fatty acid derivatives of amines, long chain fatty esters, or long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides.

[0117] In one embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment, the long chain fatty acid ester may be a monoester or a diester or a mixture thereof, and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0118] Other performance additives such as corrosion inhibitors include those described in U.S. Pub. No. 20050038319, octyl octanamide, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment, the corrosion inhibitors include a Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. Synalox® corrosion inhibitors are described in a product brochure, Form No. 118-01453-0702 AMS, entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications," published by The Dow Chemical Company.

[0119] Metal deactivators including derivatives of benzotriazoles (such as tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and copolymers of ethyl acrylate and 2-ethylhexylacrylate and vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides may be useful.

[0120] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, and polyacrylamides.

[0121] In different embodiments, the lubricating composition may have a composition as described in Table 1:

Table 1: Example Lubricating Compositions

Additive	Embodiments (wt %)		
	A	B	C
Exemplary Sulfonated Dispersant Viscosity Modifier	0.05 to 10	0.2 to 3	0.5 to 2
Dispersant	0.05 to 12	0.75 to 8	0.5 to 6
Overbased Detergent	0 or 0.05 to 15	0.1 to 10	0.2 to 8
Antioxidant	0 or 0.05 to 15	0.1 to 10	0.5 to 5

(continued)

Additive	Embodiments (wt %)		
	A	B	C
Antiwear Agent	0 or 0.05 to 15	0.1 to 10	0.3 to 5
Friction Modifier	0 or 0.05 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 or 0.05 to 10	0.5 to 8	1 to 6
Any Other Performance Additiv	0 or 0.05 to 10	0 or 0.05 to 8	0 or 0.05 to 6
Oil of Lubricating Viscosity	Balance to 100	Balance to 100	Balance to 100

[0122] The sulfonated dispersant viscosity modifier may be present in embodiments (D) at 0.1 to 8 wt %, or (E) 1 to 7 wt %, or (F) 2 to 6 wt %, or (G) 0.1 to 2 wt %, or (H) 0.3 to 1.2 wt % of the lubricating composition, with the amount of dispersant, overbased detergent, antioxidant, antiwear agent, friction modifier, viscosity modifier, any other performance additive and an oil of lubricating viscosity in amounts shown in the table above for embodiments (A) to (C).

Industrial Applications

[0123] In one embodiment, a method of lubricating an internal combustion engine includes supplying to the internal combustion engine a lubricating composition as disclosed herein. Generally, the lubricating composition is added to the lubricating system of the internal combustion engine, which then delivers the lubricating composition to the critical parts of the engine, during its operation, that require lubrication.

[0124] In one embodiment, a use of the dispersant viscosity modifier described herein to improve film thickness and/or antiwear performance of a lubricating composition is provided. These improvements can be considered in addition to the dispersancy and viscosity control performance expected from a dispersant viscosity modifier.

[0125] The lubricating compositions described above may be utilized in an internal combustion engine. The engine components may have a surface of steel or aluminum (typically a surface of steel), and may also be coated for example, with a diamond like carbon (DLC) coating. An aluminum surface may comprise an aluminum alloy that may be a eutectic or hyper-eutectic aluminum alloy (such as those derived from aluminum silicates, aluminum oxides, or other ceramic materials). The aluminum surface may be present on a cylinder bore, cylinder block, or piston ring formed of an aluminum alloy or aluminum composite.

[0126] 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).

[0127] In one embodiment, the internal combustion engine may be a diesel fuelled engine (such as a heavy duty diesel engine), a gasoline fuelled engine, a natural gas fuelled engine or a mixed gasoline/alcohol fuelled engine. In one embodiment, the internal combustion engine may be a diesel fuelled engine and in another embodiment a gasoline fuelled engine. In one embodiment, the internal combustion engine may be a biodiesel fuelled engine. The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines. In one embodiment the internal combustion engine is a gasoline direct injection (GDI) engine.

[0128] The internal combustion engine is distinct from gas turbine. In an internal combustion engine, individual combustion events which through the rod and crankshaft translate from a linear reciprocating force into a rotational torque. In contrast, in a gas turbine (which may also be referred to as a jet engine) it is a continuous combustion process that generates a rotational torque continuously without translation and can also develop thrust at the exhaust outlet. These differences result in the operation conditions of a gas turbine and internal combustion engine different operating environments and stresses.

[0129] The lubricating composition for an internal combustion engine may be suitable for use as an engine lubricant irrespective of the sulfur, phosphorus or sulfated ash (ASTM D874) content. The sulfur content of the lubricating composition, which is particularly suited to use as an engine oil lubricant, 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 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content may be 2 wt % or less, or 1.5 wt % or less, or 1.1 wt % or less, or 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.4 wt % or less. In one embodiment, the sulfated ash content may be 0.05 wt % to 0.9 wt %, or 0.1 wt %

to 0.2 wt % or to 0.45 wt %. In one embodiment, the lubricating composition may be an engine oil, wherein the lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, (iii) a sulfated ash content of 1.5 wt % or less, or combinations thereof.

EXAMPLES

[0130] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the invention, they are not intended to limit it.

[0131] As used herein kinematic viscosity is measured at 100°C (KV_{100}), according to the method of ASTM D445 - 12, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)", ASTM International, West Conshohocken, PA, DOI: 10.1520/D0445-12. This test method specifies a procedure for the determination of the kinematic viscosity, of liquid petroleum products by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. It may be noted that 1 mm^2/s = 10^{-6} m^2/s = 1 cSt.

[0132] The viscosity index (VI) is determined according to ASTM D2270-10e1, "Standard Practice for Calculating Viscosity Index From Kinematic Viscosity at 40 and 100°C," DOI: 10.1520/D2270-10E01.

[0133] The High Temperature/High Shear rate viscosity, HTHS (150°C), of a lubricating composition containing the exemplary dispersant viscosity modifier is determined herein according to the procedure defined in ASTM D4683-10, "Standard Test Method for Measuring Viscosity of New and Used Engine Oils at High Shear Rate and High Temperature by Tapered Bearing Simulator Viscometer at 150°C," ASTM International, West Conshohocken, PA. This test method determines the viscosity of an oil at 150 °C and 1.0 x 10^6 s^{-1} using a viscometer having a slightly tapered rotor and stator called the Tapered Bearing Simulator (TBS) Viscometer. Unless otherwise noted, HTHS values are determined by this method and are reported in centipoise (cP). 1 centipoise = 1 mPa-s. (Other suitable methods to measure HTHS viscosity are ASTM D4741, D5481 or CEC L-36-90 but are not used herein unless specifically noted).

[0134] Low temperature flow to an engine oil pump or oil distribution system is simulated by measuring engine starting viscosity in centipoise according to ASTM D5293 - 14, "Standard Test Method for Apparent Viscosity of Engine Oils and Base Stocks Between -5°C and -35°C Using Cold-Cranking Simulator," DOI: 10.1520/D5293-14.

Example 1: Preparation of a succinimide intermediate

[0135] A succinimide intermediate is prepared by adding to a 3 L round bottom flask equipped with a mechanical stirrer, thermowell, nitrogen inlet, Dean-Stark trap and Friedrich's condenser, 852.0 grams of a maleated ethylene propylene copolymer, commercially available from Mitusi as Lucant™ A-5320H, and 852.0 g of diluent oil. The material is heated to 110°C with stirring and nitrogen purge. 25.8 grams of 3-aminopropanol is added to the mixture, resulting in the formation of a gel. Xylenes (54 g) are added to the flask with continued heating resulting in the gel eventually melting after about 20 minutes of agitation. The solution is then warmed to 175°C and agitated for 4.0 hours. The solution is cooled to 165°C and held an additional 1.5 hours at this temperature. The resulting polymer is stripped of solvents under deep vacuum at 165°C for 40 minutes. 1712.0 grams of the succinimide intermediate, appearing as a viscous yellow liquid, is recovered.

Example 2: Preparation of a Maleated Ethylene Propylene Alkyl Sulfonic Acid Dispersant Viscosity Modifier

[0136] A dispersant viscosity modifier is prepared by adding to a 2 L round bottom flask equipped with a mechanical stirrer, thermowell, nitrogen inlet, Dean-Stark trap and Friedrich's condenser, 300.0 grams of the succinimide intermediate of Example 1 and 328.2 g of diluent oil. The solution is heated to 110°C with agitation and nitrogen purge. Then, 11.1 grams of butanesultone are added, followed by toluene (50 ml). The solution is agitated at 125°C for 2 hours, then the temperature increased to 150°C for 6 hours. Solvent is then removed under deep vacuum at 150°C for 30 min to yield 625.0 grams of product, appearing as a viscous liquid. The resulting dispersant viscosity modifier is referred to below as 3.5% MAA alkyl sulfonic acid.

Example 3 Preparation of a Maleated Ethylene Propylene Aryl Sulfonate Salt Dispersant Viscosity Modifier

[0137] A dispersant viscosity modifier is prepared by adding to a 2 L round bottom flask equipped with a mechanical stirrer, thermowell, nitrogen inlet, Dean-Stark trap and Friedrich's condenser, 430.0 grams of maleated ethylene propylene copolymer (Lucant™ A-5320H) and 486.0 g of diluent oil. The solution is heated to 120°C with agitation and nitrogen purge for 1 hour. 31.7 grams of tributylamine is added to the flask followed by 27.2 grams of sulfanilic acid. The flask is heated to 160°C for 7.5 hours. Additional tributylamine (31.7 g) is added to the flask with agitation at 160°C for 6.75 hours. Excess tributylamine is removed under deep vacuum at 160°C for 3 hours. 546.8 g of diluent oil is added to the

flask, providing 1430.3 g of product as a dark viscous liquid. The resulting dispersant viscosity modifier is referred to below as 3.5% MAA aryl tributylammonium sulfonate.

[0138] The product of Example 3 may be washed with aqueous acid to facilitate a cation exchange from a trialkylammonium ion to an H^+ ion, effectively converting the salt to an acid, as described in Example 4.

Example 4: Preparation of a Maleated Ethylene Propylene Aryl Sulfonic Acid Dispersant Viscosity Modifier

[0139] A dispersant viscosity modifier is prepared by adding to a 5 L round bottom flask equipped with a mechanical stirrer, thermowell, nitrogen inlet, Dean-Stark trap and Friedrich's condenser, 1372.5 grams of the succinimide intermediate of Example 3 and 1372.5 g of toluene. Flask contents are heated to 40 °C and stirred until homogenous.

[0140] A 1 N solution of H_2SO_4 is prepared and charged (274.5 ml) to the flask. Contents of the flask are stirred for 20 min at 40 °C. Flask contents are transferred to a separatory funnel and the phases allowed to separate. The aqueous phase is removed and the organic phase is returned to the flask. A 2 N solution of H_2SO_4 is prepared and charged (137.3 ml) to the flask. Contents of the flask are stirred for 20 min at 40°C. Contents of the flask are transferred to a separatory funnel and the phases allowed to separate. The aqueous phase is removed and the organic phase is returned to the flask. 2 N H_2SO_4 (137.3 ml) is charged a second time to the flask. Contents of the flask are stirred for 20 min at 40°C. Contents of the flask are transferred to a separatory funnel and the phases allowed to separate. The aqueous phase is removed and the organic phase is returned to the flask. 2 N H_2SO_4 (137.3 ml) is again charged to the flask. Contents of the flask are stirred for 20 min at 40°C. Contents of the flask are transferred to a separatory funnel and the phases allowed to separate. The aqueous phase is removed and the organic phase is returned to the flask.

[0141] Saturated aqueous NaCl (150 ml) is charged to the flask. Contents of the flask are stirred for 20 min at 40°C. Contents of the flask are transferred to a separatory funnel and the phases allowed to separate. The aqueous phase is removed and the organic phase is returned to the flask. Saturated aqueous NaCl (150 ml) is again charged to the flask. Contents of the flask are stirred for 20 min at 40°C. Contents of the flask are transferred to a separatory funnel and the phases allowed to separate. The aqueous phase is removed and the organic phase is returned to the flask. The contents of the flask are heated to 120°C resulting in the collection of water and toluene. The temperature is increased to 135°C and held, resulting in the collection of additional toluene. The temperature is increased to 150°C and held, resulting in the collection of additional toluene. Vacuum is applied to -250 mmHg (-33331 Pascal) at 150°C, resulting in the collection of toluene. Vacuum is further applied to 10-15 mmHg (1333-2000Pa) at 150°C, resulting in the collection of additional toluene. Vacuum is released and the product is filtered. The resulting product is a dark viscous oil.

Preparation of Lubricating Compositions

1. Passenger Car Engine Oil formulation

[0142] The dispersant viscosity modifier of Example 2 is prepared at 25 wt% polymer in 75 wt% diluent oil. This is blended into a group III base oil in amounts by weight to form lubricating compositions, as summarized in Table 2 below. Comparative Example 5 includes an amine-free dispersant viscosity modifier (a polymethacrylate (84% C12-15 methacrylate/16% methyl methacrylate), with a weight average molecular weight of 330,000). Examples 6 and 7 contain the dispersant viscosity modifiers of Examples 2 and 4 respectively as well as some of the amine-free dispersant viscosity modifier used in Example 5.

[0143] Each of the blends is designed to have nearly equivalent kinematic viscosities at 100°C (KV_{100}) to allow for direct comparison:

KV_{100} about 8.5 cSt,
VI about 222,
HTHS (150°C) about 2.6cP,
D5293 (-35°C) about 3700 cP.

TABLE 2: Treat Rates (wt % of Lubricating Composition)

Lubricating composition	Comparative Example 5	Example 6	Example 7
Example 2 (3.5% MAA all sulfonic acid)	-	1.44 (0.36% active)	
Example 4 (3.5 % MAA aryl sulfonic acid)	-		1.20 % (0.36 % active)

(continued)

Lubricating composition	Comparative Example 5	Example 6	Example 7
amine-free dispersant viscosity modifier	6.01 % (2.16 % active)	5.01% (1.80% active)	5.01 % (1.80 % active)
Pour Point Depressant	0.1 %	0.1 %	0.1 %
Dispersant-Inhibitor Package	9.18 %	9.18 %	9.18 %
Base Oil	balance	balance	balance

[0144] The data in parenthesis is the amount of actives for each component. The weight % actives are based on the entire composition. The Dispersant-Inhibitor Package may include some oil. The lubricating compositions of Examples 5-7 include about 0.75% zinc dialkyldithiophosphate (ZDDP) (which delivers about 0.076% phosphorus to the lubricating composition).

Friction Properties

[0145] Friction properties were determined using a Mini Traction Machine (MTM). The lubricants are evaluated in a commercially-available mini-traction tester machine. A simulated concentrated contact forms between a steel ball and a steel disc (Smooth disk). Traction measurements are made at a rolling speed (of the steel ball) of 2.5 m/s and a 20% slide to roll ratio. The temperature was 140 °C and load was 72N. FIGURE 1 shows the Stribeck curve obtained.

[0146] Given the parameters of this particular experiment, the performance of the 3.5% MAA alkyl sulfonic acid in the finished fluid can be measured in all three regions of the Stribeck curve. The area of interest is the mixed regime, which can be found between the two vertical lines. The mixed regime is indicative of the durability of the friction modifier characteristics of the dispersant viscosity modifier, as determined by the Sequence VID engine test (ASTM D7589), which is heavily weighted towards the mixed regime.

[0147] From the MTM data, the 3.5% MAA alkyl sulfonic acid outperformed the baseline (Example 5) formulation.

2. Heavy Duty Engine Oil formulation

[0148] For this study, comparative Example 8 includes a conventional dispersant viscosity modifier (32 wt % active polymer, 68 wt % oil). In the blends of Examples 9 and 10, this replaced with either 3.5% MAA alkyl sulfonic acid (prepared at 25 wt % polymer, 75 wt % oil) or 3.5% MAA aryl tributylammonium sulfonate (prepared at 29.7 wt % polymer, 70.3 wt % oil) at a treat rate to obtain the following viscometric parameters:

Kv_{100} about 12.1-11.4 cSt

VI about 145

HTHS (150 °C) $\geq$ 3.5 cP

D5293 (-25°C) cold crankabout 5800-6600 cP

[0149] The treat rates for each NOCH-S dispersant viscosity modifier in the base oil are shown in TABLE 3.

TABLE 3: Treat Rates (wt % of Lubricating Composition)

Lubricating composition	Comparative Example 8	Example 9	Example 10
Conventional dispersant viscosity modifier	2.05 wt % (0.66 wt % active)		
Example 2 (3.5 % MAA alkyl sulfonic acid)		2.80 wt % (0.70 wt % active)	
Example 4 (3.5 % MAA aryl sulfonic acid)			0.60 (0.18 wt % active)

(continued)

Lubricating composition	Comparative Example 8	Example 9	Example 10
Viscosity Modifier	3.9 wt % (0.49 wt % active	3.9 (0.49 wt % actives)	3.9 (0.49 wt % actives)
Pour Point Depressant	0.2	0.2	0.2
Dispersant-Inhibitor Package	14.85	14.85	14.85
Base Oil	Balance	Balance	Balance

[0150] The weight % actives are also based on the entire composition. The lubricating compositions of Examples 8-10 include about 1% zinc dialkyldithiophosphate (ZDDP) (which delivers about 0.11% phosphorus to the composition). The compositions include about 1% sulfated ash and have a TBN of about 8.5.

[0151] The film thickness of the blends in TABLE 3, when subjected to boundary, mixed and hydrodynamic lubrication conditions is measured by an elastohydrodynamic (EHD) ball on plate rig. Briefly, a chamber is flooded with one of the blends from TABLE 3. The chamber is equipped with a ball that rolls on a glass plate and a chromium spacer. By digital analysis of the interference pattern of reflected light shined on the ball in contact with the plate, the film thickness is measured to the nanometer scale. The experiment is performed at 140°C over a variety of rolling speeds. Conditions are as follows: 0.5 GPa Hertz Pressure, 17 N.

[0152] FIGURE 2 shows the EHD data obtained. It can be seen that the Example 9 and 10 NOCH-S DVMs both form a thicker film, as compared to comparative Example 8.

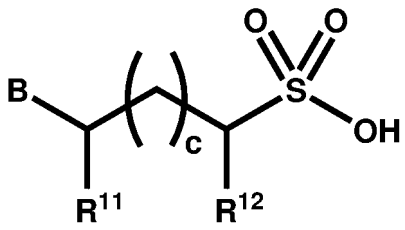
[0153] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of 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.

[0154] 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.

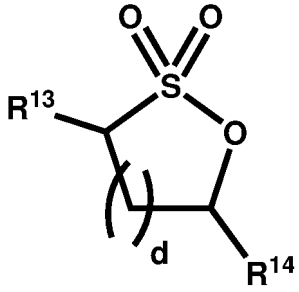
Claims

1. A lubricating composition comprising:

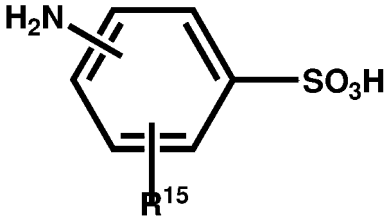
an oil of lubricating viscosity; and
at least 0.05 wt. % of an oil-soluble dispersant viscosity modifier comprising an olefin-based polymer backbone and at least one pendent functional group selected from alkyl and aryl sulfonate salts, alkyl and aryl sulfonic acids, and combinations thereof, the olefin-based polymer backbone comprising an ethylene-olefin-based copolymer, each of the at least one pendent functional group being independently attached to the olefin-based polymer backbone by a linking group, the at least one pendent functional group comprising a sulfonate moiety, wherein the at least one pendent functional group is derived from a sulfonated hydrocarbyl compound selected from the group consisting of:



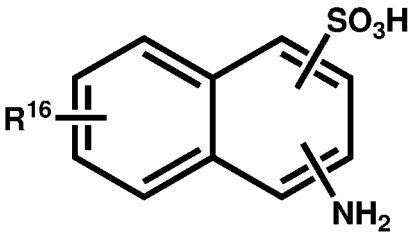
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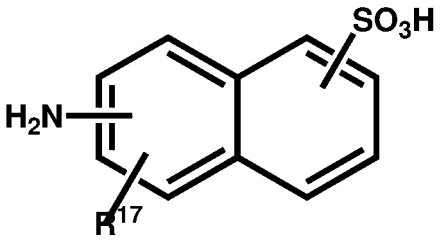
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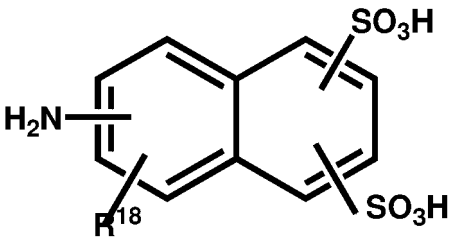
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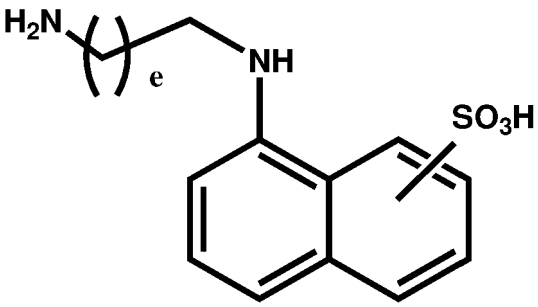
(VII),



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(X),

where c is from 1-10,
d is from 1-10,
e is at least 1,
B is NH_2 or OH,
R^{11}, Ft^{12}, R^{13} and R^{14} are independently H or a C_1 to C_{30} alkyl group, and
R^{15}, R^{16}, R^{17}, and R^{18} are independently selected from H, OH, NH_2, alkyl groups, and alkoxy groups

2. The lubricating composition of claim 1, wherein the sulfonate moiety is spaced from the olefin-based polymer backbone by a C_4-C_{24} hydrocarbyl group.

3. The lubricating composition of claim 1 or 2, wherein the at least one pendent functional group comprises a C_3-C_{24} alkyl chain which spaces the sulfonate moiety from the polymer backbone.

4. The lubricating composition of any one of claims 1-3, wherein at least some of the linking groups are derived from an ethylenically unsaturated carboxylic acid monomer.

5. The lubricating composition of claim 2 or 3, wherein the linking groups are attached to the pendent groups by linker units derived from at least one of hydroxyl alkyl amines, alkylene polyamines, and polyols.

6. The composition of claim 5, wherein at least some of the linking groups are derived from maleic anhydride and at least some of the linker units are derived from a hydroxyl alkyl amine.

7. The lubricating composition of any one of claims 1-6, wherein the sulfonate moiety comprises a sulfonate salt which includes a cation of the general form -($NR^3R^4R^5$), where R^3, R^4, and R^5 are independently selected from H and C_1 to C_{30} alkyl groups.

8. The lubricating composition of any one of claims 1-7, wherein a ratio by weight of linking groups to the polymer backbone in the dispersant viscosity modifier is at least 2:100.

9. The lubricating composition of any one of claims 1-8, wherein a ratio by weight of linking groups to the polymer backbone in the dispersant viscosity modifier is up to 10:100.

10. The lubricating composition of any one of claims 1-9, wherein the dispersant viscosity modifier has an HLB value of up to 10,
where HLB = 20*M*h*/M, where M*h* is the molecular mass of the hydrophilic portion of the molecule and M is the molecular mass of the whole molecule.

11. The lubricating composition of any one of claims 1-10, wherein ethylene-olefin-based copolymer comprises at least 10 mole percent ethylene.

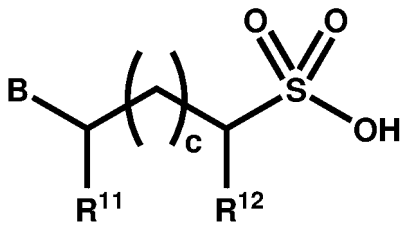
12. The lubricating composition of any one of claims 1-11, wherein the olefin-based polymer backbone has a number average molecular weight, as measured by gel permeation chromatography, using a polystyrene standard, of greater of at least 1000.

13. The lubricating composition of any one of claims 1-12, wherein the composition further comprises at least one of a dispersant, a detergent, an overbased detergent, an antioxidant a viscosity modifier, a friction modifier, a corrosion inhibitor, a pour point depressant, a seal swell agent, a demulsifier, and an antiwear agent.

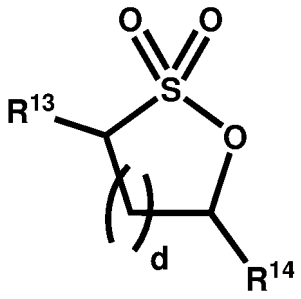
14. Use of the dispersant viscosity modifier of any of claims 1-13 for improving film thickness and/or antiwear performance of an engine lubricating composition.

15. A process for making a lubricating composition comprising:

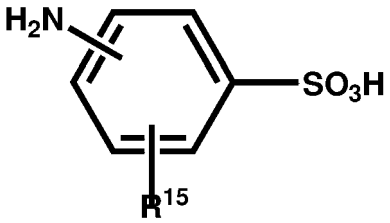
(i) providing an olefin-based polymer backbone with one or more acylating linking groups, each independently attached along the polymer backbone, the olefin-based polymer backbone comprising an ethylene-olefin-based copolymer;
(ii) optionally, reacting each acylating group with a hydroxy alkyl amine, an alkylene polyamine, a polyol, or a combination thereof, resulting in an olefin-based polymer with one or more linker units each independently attached along the polymer backbone;and
(iii) reacting each linking group or linker unit with a hydrocarbyl sulfonate compound selected from sulfonate salts and sulfonic acids, resulting in a dispersant viscosity modifier comprising one or more pendent hydrocarbyl sulfonate groups each independently attached to the olefin-based polymer, wherein the sulfonated hydrocarbyl compound is selected from the group consisting of:



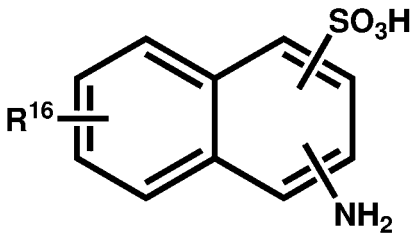
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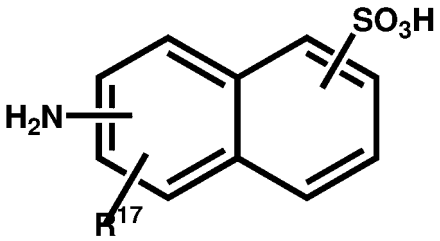
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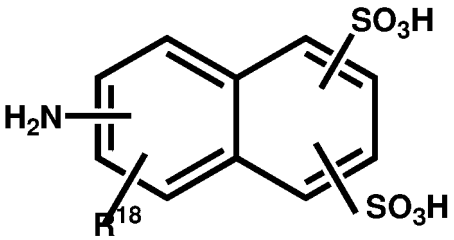
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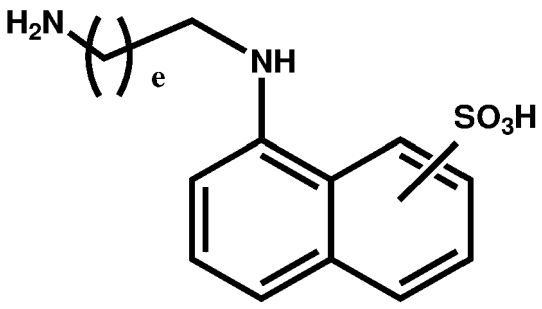
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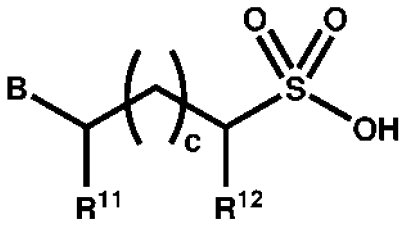
where c is from 1-10,

d is from 1-10,
e is at least 1,
B is NH_2 or OH,
R^{11}, R^{12}, R^{13} and R^{14} are independently H or a C_1 to C_{30} alkyl group, and
R^{15}, R^{16}, R^{17}, and R^{18} are independently selected from H, OH, NH_2, alkyl groups, and alkoxy groups.

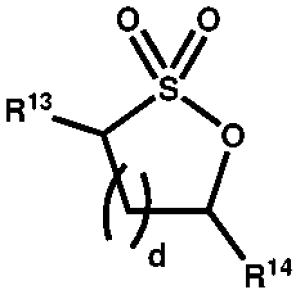
Patentansprüche

1. Schmierzusammensetzung, umfassend:

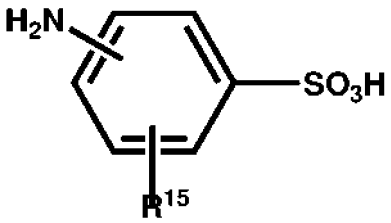
ein Öl mit Schmierviskosität; und
mindestens 0,05 Gew.-% eines öllöslichen dispergierenden Viskositätsmodifizierers, umfassend ein Polymerrückgrat auf Olefinbasis und mindestens eine seitenständige funktionelle Gruppe, ausgewählt aus Alkyl- und Arylsulfonatsalzen, Alkyl- und Arylsulfonsäuren und Kombinationen davon, das Polymerrückgrat auf Olefinbasis umfassend ein Copolymer auf Ethylenolefinbasis, wobei jede der mindestens einen seitenständigen funktionellen Gruppe an das Polymerrückgrat auf Olefinbasis durch eine Verknüpfungsgruppe unabhängig angelagert ist, die mindestens eine seitenständige funktionelle Gruppe umfassend ein Sulfonatmolekülteil, wobei die mindestens eine seitenständige funktionelle Gruppe von einer sulfonierten Hydrocarbylverbindung abstammt, die aus der Gruppe ausgewählt ist, bestehend aus:



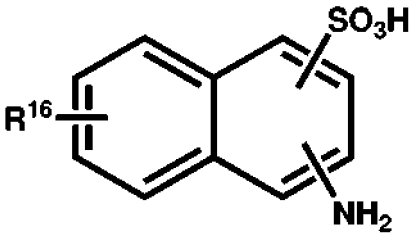
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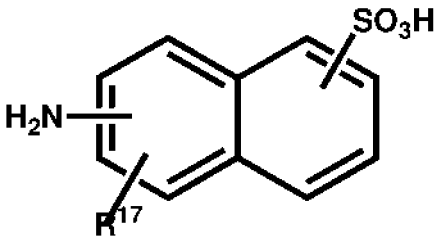
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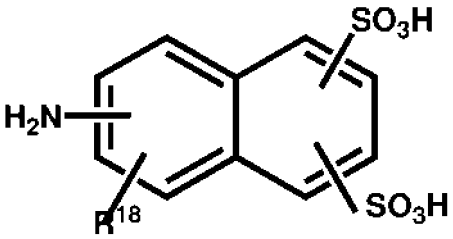
(VI),



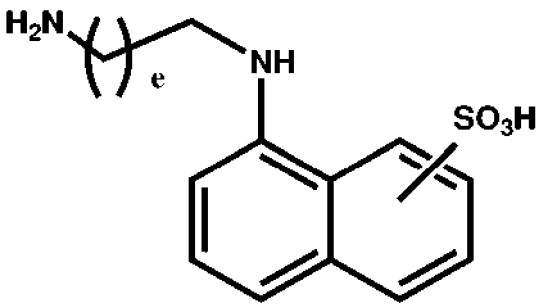
(VII),



(VIII),



(IX),



(X),

wobei c von 1-10 ist,
d von 1-10 ist,
e mindestens 1 ist,
B NH_2 oder OH ist,
R^{11}, R^{12}, R^{13} und R^{14} unabhängig H oder eine C_1- bis C_{30}-Alkylgruppe sind, und
R^{15}, R^{16}, R^{17} und R^{18} unabhängig aus H, OH, NH_2, Alkylgruppen und Alkoxygruppen ausgewählt sind

2. Schmierzusammensetzung nach Anspruch 1, wobei der Sulfonatmolekülteil von dem Polymerrückgrat auf Olefinbasis durch eine C_4-C_{24}-Hydrocarbylgruppe beabstandet ist.

3. Schmierzusammensetzung nach Anspruch 1 oder 2, wobei die mindestens eine seitenständige funktionelle Gruppe eine C_3-C_{24}-Alkylkette umfasst, die den Sulfonatmolekülteil von dem Polymerrückgrat beabstandet.

4. Schmierzusammensetzung nach einem der Ansprüche 1 bis 3, wobei mindestens einige der Verknüpfungsgruppen von einem ethylenisch ungesättigten Carbonsäuremonomer abstammen.

5. Schmierzusammensetzung nach Anspruch 2 oder 3, wobei die Verknüpfungsgruppen an die seitenständigen Gruppen durch Verknüpfereinheiten, die von mindestens einem von Hydroxylalkylaminen, Alkylenpolyaminen und Polyolen abstammen, angelagert sind.

6. Zusammensetzung nach Anspruch 5, wobei mindestens einige der Verknüpfungsgruppen von Maleinsäureanhydrid abstammen und mindestens einige der Verknüpfereinheiten von einem Hydroxylalkylamin abstammen.

7. Schmierzusammensetzung nach einem der Ansprüche 1 bis 6, wobei der Sulfonatmolekülteil ein Sulfonatsalz umfasst, das ein Kation der allgemeinen Form - ($NR^3R^4R^5$) beinhaltet, wobei R^3, R^4 und R^5 unabhängig aus H und C_1- bis C_{30}-Alkylgruppen ausgewählt sind.

8. Schmierzusammensetzung nach einem der Ansprüche 1 bis 7, wobei ein Gewichtsverhältnis von Verknüpfungsgruppen zu dem Polymerrückgrat in dem dispergierenden Viskositätsmodifizierer mindestens 2 : 100 ist.

9. Schmierzusammensetzung nach einem der Ansprüche 1 bis 8, wobei ein Gewichtsverhältnis von Verknüpfungsgruppen zu dem Polymerrückgrat in dem dispergierenden Viskositätsmodifizierer bis zu 10 : 100 ist.

10. Schmierzusammensetzung nach einem der Ansprüche 1 bis 9, wobei der dispergierende Viskositätsmodifizierer einen HLB-Wert von bis zu 10 aufweist,
wobei HLB = 20*M*h*/M, wobei M*h* die Molekularmasse des hydrophilen Anteils des Moleküls ist und M die Molekülmasse des gesamten Moleküls ist.

11. Schmierzusammensetzung nach einem der Ansprüche 1 bis 10, wobei das Copolymer auf Ethylenolefinbasis mindestens 10 Molprozent Ethylen umfasst.

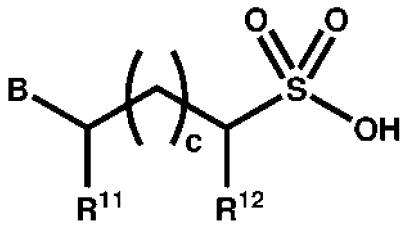
12. Schmierzusammensetzung nach einem der Ansprüche 1 bis 11, wobei das Polymerrückgrat auf Olefinbasis ein Zahlenmittel einer Molekülmasse, wie durch Gelpermeationschromatographie unter Verwendung eines Polystyrolstandards gemessen, von mehr als mindestens 1000 aufweist.

13. Schmierzusammensetzung nach einem der Ansprüche 1 bis 12, wobei die Zusammensetzung ferner mindestens eines von einem Dispergiermittel, einem Detergens, einem überbasischen Detergens, einem Antioxidans, einem Viskositätsmodifizierer, einem Reibungsmodifizierer, einem Korrosionsinhibitor, einem Stockpunkterniedriger, einem Dichtungsquellmittel, einem Demulgator und einem Antiverschleißmittel umfasst.

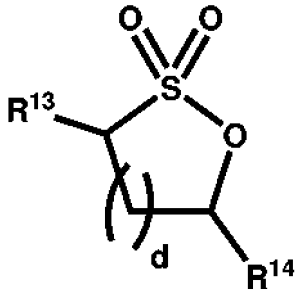
14. Verwendung des dispergierenden Viskositätsmodifizierers nach einem der Ansprüche 1 bis 13 zum Erhöhen einer Filmdicke und/oder Antiverschleißleistung einer Motorschmierzusammensetzung.

15. Verfahren zum Herstellen einer Schmierzusammensetzung, umfassend:

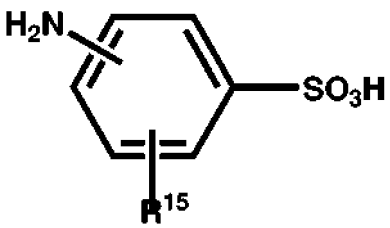
(i) Bereitstellen eines Polymerrückgrates auf Olefinbasis mit einer oder mehreren Acylierungsverknüpfungsgruppen, die jeweils unabhängig entlang des Polymerrückgrates angelagert sind, das Polymerrückgrat auf Olefinbasis umfassend ein Copolymer auf Ethylenolefinbasis;
(ii) optional, Reagieren jeder Acylierungsgruppe mit einem Hydroxyalkylamin, einem Alkylenpolyamin, einem Polyol oder einer Kombination davon, resultierend in einem Polymer auf Olefinbasis mit einer oder mehreren Verknüpfereinheiten, die jeweils unabhängig entlang des Polymerrückgrates angelagert sind; und
(iii) Reagieren jeder Verknüpfungsgruppe oder Verknüpfereinheit mit einer Hydrocarbylsulfonatverbindung, ausgewählt aus Sulfonatsalzen und Sulfonsäuren, resultierend in einem dispergierenden Viskositätsmodifizierer, umfassend eine oder mehrere seitenständige Hydrocarbylsulfonatgruppen, die jeweils unabhängig an das Polymer auf Olefinbasis angelagert sind, wobei die sulfonierte Hydrocarbylverbindung aus der Gruppe ausgewählt ist, bestehend aus:



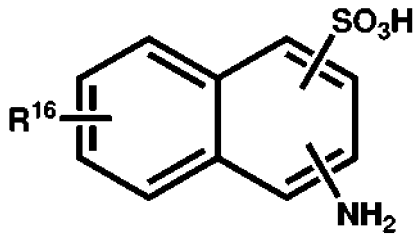
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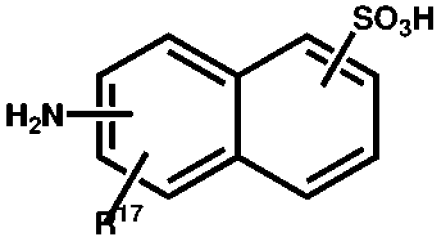
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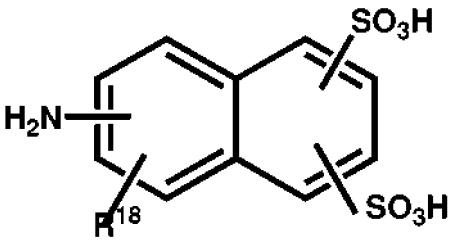
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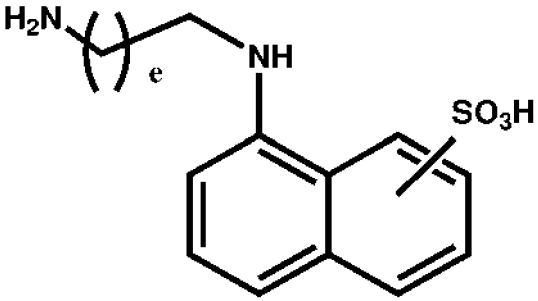
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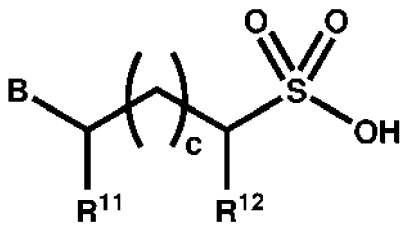
wobei c von 1-10 ist,

d von 1-10 ist,
e mindestens 1 ist,
B NH_2 oder OH ist,
R^{11}, R^{12}, R^{13} und R^{14} unabhängig voneinander H oder eine C_1- bis C_{30}-Alkylgruppe sind, und
R^{15}, R^{16}, R^{17} und R^{18} unabhängig aus H, OH, NH_2, Alkylgruppen und Alkoxygruppen ausgewählt sind.

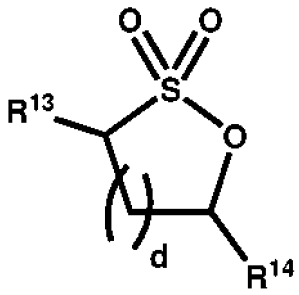
Revendications

1. Composition lubrifiante comprenant :

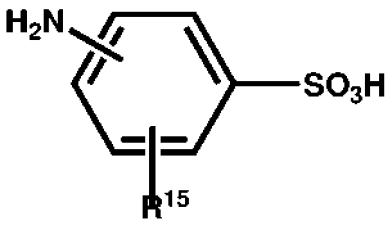
une huile de viscosité lubrifiante ; et
au moins 0,05 % en poids d'un modificateur de viscosité dispersant soluble dans l'huile comprenant un squelette polymère à base d'oléfine et au moins un groupe fonctionnel pendant choisi parmi les sels d'alkyl et d'aryl sulfonate, les acides alkyl et aryl sulfoniques, et des combinaisons de ceux-ci, le squelette polymère à base d'oléfine comprenant un copolymère à base d'éthylène-oléfine, chacun du au moins un groupe fonctionnel pendant étant attaché indépendamment au squelette polymère à base d'oléfine par un groupe de liaison, l'au moins un groupe fonctionnel pendant comprenant une fraction sulfonate, dans laquelle l'au moins un groupe fonctionnel pendant est dérivé d'un composé hydrocarbyle sulfoné choisi dans le groupe constitué par :



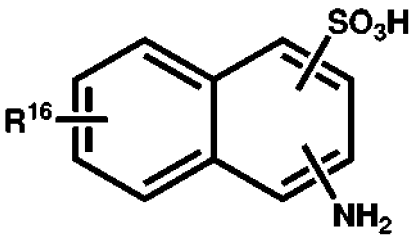
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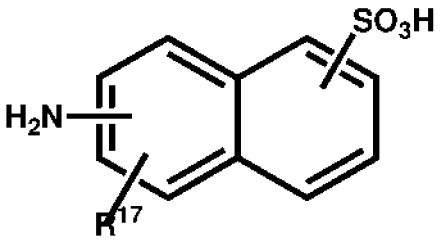
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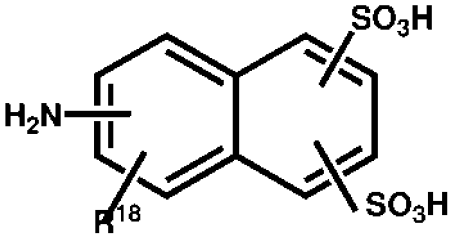
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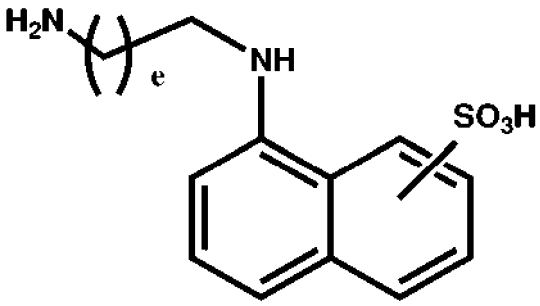
(VII),



(VIII),



(IX),



(X),

dans laquelle c va de 1 à 10,

d va de 1 à 10,
e vaut au moins 1,
B est NH_2 ou OH,
R^{11}, R^{12}, R^{13} et R^{14} sont indépendamment H ou un groupe alkyle en C_1 à C_{30}, et
R^{15}, R^{16}, R^{17} et R^{18} sont choisis indépendamment parmi H, OH, NH_2, des groupes alkyle et des groupes alcoxy.

2. Composition lubrifiante selon la revendication 1, dans laquelle la fraction sulfonate est espacée du squelette polymère à base d'oléfine par un groupe hydrocarbyle en C_4-C_{24}.

3. Composition lubrifiante selon la revendication 1 ou 2, dans laquelle l'au moins un groupe fonctionnel pendant comprend une chaîne alkyle en C_3-C_{24} qui espace la fraction sulfonate du squelette polymère.

4. Composition lubrifiante selon l'une quelconque des revendications 1 à 3, dans laquelle au moins une partie des groupes de liaison sont dérivés d'un monomère d'acide carboxylique à insaturation éthylénique.

5. Composition lubrifiante selon la revendication 2 ou 3, dans laquelle les groupes de liaison sont attachés aux groupes pendants par des unités de liaison dérivées d'hydroxylalkylamines et/ou d'alkylènepolyamines et/ou de polyols.

6. Composition selon la revendication 5, dans laquelle au moins une partie des groupes de liaison sont dérivés de l'anhydride maléique et au moins une partie des unités de liaison sont dérivées d'une hydroxylalkylamine.

7. Composition lubrifiante selon l'une quelconque des revendications 1 à 6, dans laquelle la fraction sulfonate comprend un sel sulfonate qui comporte un cation de la forme générale -($NR^3R^4R^5$), dans laquelle R^3, R^4 et R^5 sont indépendamment choisis parmi H et les groupes alkyle en C_1 à C_{30}.

8. Composition lubrifiante selon l'une quelconque des revendications 1 à 7, dans laquelle un rapport en poids des groupes de liaison au squelette polymère dans le modificateur de viscosité dispersant est d'au moins 2:100.

9. Composition lubrifiante selon l'une quelconque des revendications 1 à 8, dans laquelle un rapport en poids des groupes de liaison au squelette polymère dans le modificateur de viscosité dispersant va jusqu'à 10:100.

10. Composition lubrifiante selon l'une quelconque des revendications 1 à 9, dans laquelle le modificateur de viscosité dispersant présente une valeur HLB allant jusqu'à 10,
dans laquelle HLB = 20*M*h*/M, dans laquelle M*h* est la masse moléculaire de la partie hydrophile de la molécule et M est la masse moléculaire de l'ensemble de la molécule.

11. Composition lubrifiante selon l'une quelconque des revendications 1 à 10, dans laquelle le copolymère à base d'éthylène-oléfine comprend au moins 10 pour cent en moles d'éthylène.

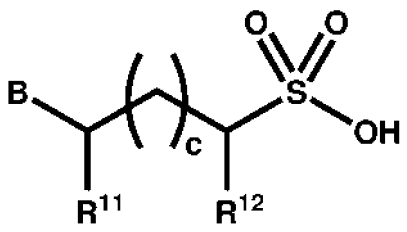
12. Composition lubrifiante selon l'une quelconque des revendications 1 à 11, dans laquelle le squelette polymère à base d'oléfine présente une masse moléculaire moyenne en nombre, telle que mesurée par chromatographie par perméation de gel, à l'aide d'un étalon de polystyrène, supérieure à au moins 1 000.

13. Composition lubrifiante selon l'une quelconque des revendications 1 à 12, dans laquelle la composition comprend en outre un dispersant et/ou un détergent et/ou un détergent surbasé et/ou un antioxydant et/ou un modificateur de viscosité et/ou un modificateur de frottement et/ou un inhibiteur de corrosion et/ou un agent abaisseur de point d'écoulement et/ou un agent de gonflement d'étanchéité et/ou un désémulsifiant et/ou un agent anti-usure.

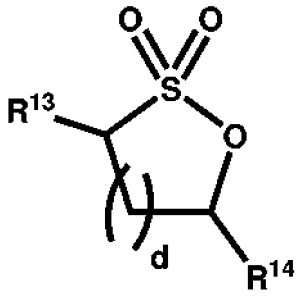
14. Utilisation du modificateur de viscosité dispersant selon l'une quelconque des revendications 1 à 13 pour l'amélioration d'une épaisseur de film et/ou des performances anti-usure d'une composition lubrifiante pour moteur.

15. Procédé de fabrication d'une composition lubrifiante comprenant :

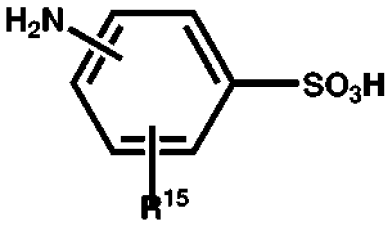
(i) la fourniture d'un squelette polymère à base d'oléfine avec un ou plusieurs groupes de liaison acylants, chacun étant attaché indépendamment le long du squelette polymère, le squelette polymère à base d'oléfine comprenant un copolymère à base d'éthylène-oléfine ;
(ii) facultativement, la réaction de chaque groupe acylant avec une hydroxyalkylamine, une alkylènepolyamine, un polyol ou une combinaison de ceux-ci, résultant en un polymère à base d'oléfine avec une ou plusieurs unités de liaison chacune attachée indépendamment le long du squelette polymère ; et
(iii) la réaction de chaque groupe de liaison ou unité de liaison avec un composé sulfonate d'hydrocarbyle choisi parmi les sels de sulfonate et les acides sulfoniques, résultant en un modificateur de viscosité dispersant comprenant un ou plusieurs groupes sulfonate d'hydrocarbyle pendants chacun indépendamment attaché au polymère à base d'oléfine, dans lequel le composé d'hydrocarbyle sulfoné est choisis dans le groupe constitué par :



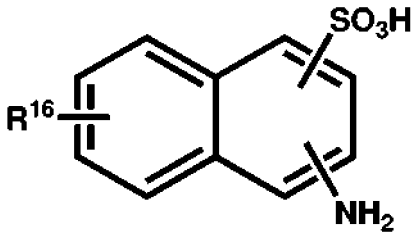
(IV),



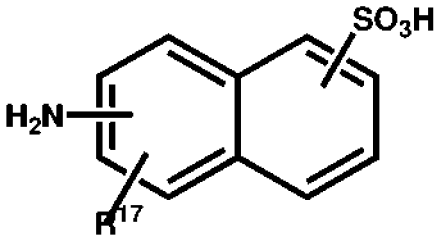
(V),



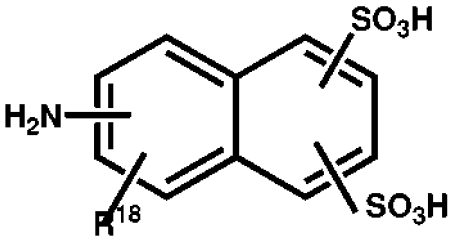
(VI),



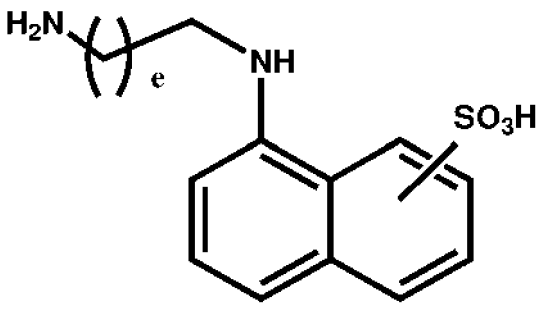
(VII),



(VIII),



(IX),



(X),

dans lequel c va de 1 à 10,

d va de 1 à 10,
e vaut au moins 1,
B est NH_2 ou OH,
R^{11}, R^{12}, R^{13} et R^{14} sont indépendamment H ou un groupe alkyle en C_1 à C_{30}, et
R^{15}, R^{16}, R^{17} et R^{18} sont choisis indépendamment parmi H, OH, NH_2, des groupes alkyle et des groupes alcoxy.

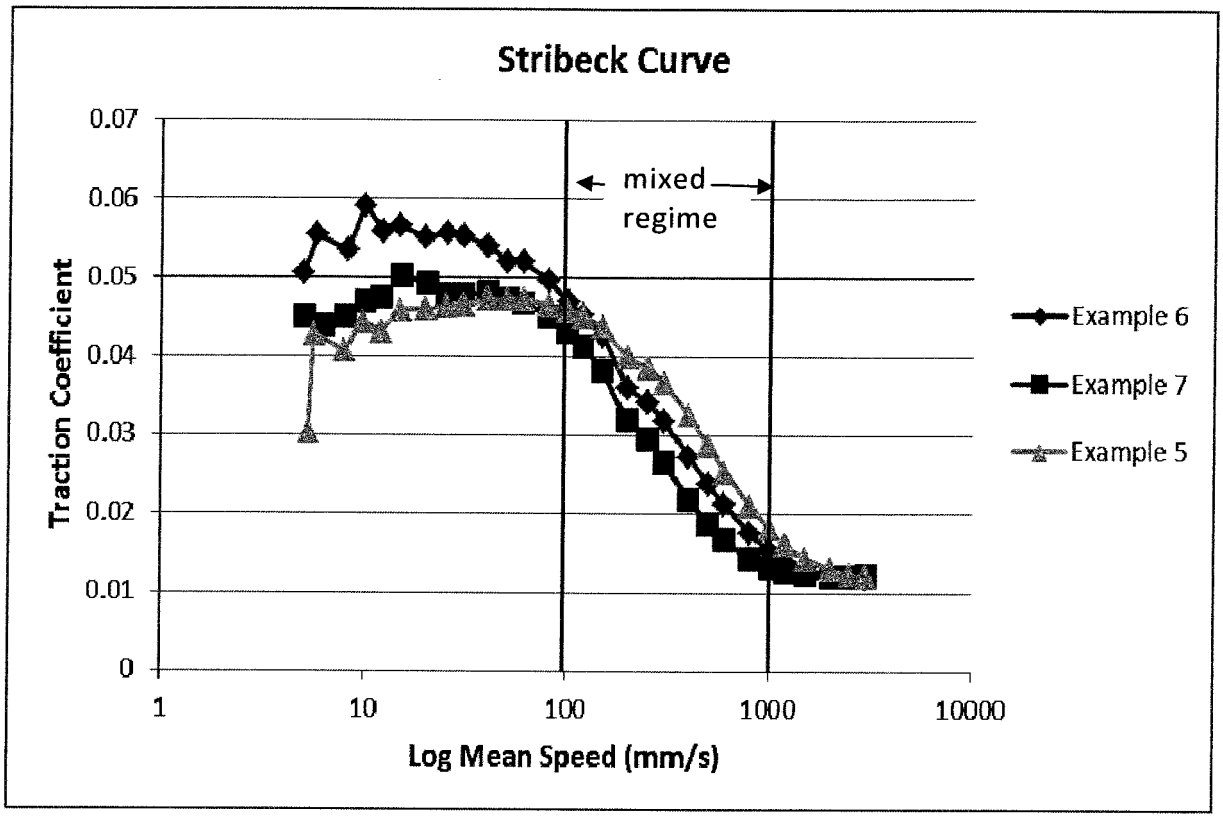

Stribeck Curve
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Traction Coefficient
mixed
regime
1
10
100
1000
10000
Log Mean Speed (mm/s)
Example 6
Example 7
Example 5

FIG. 1

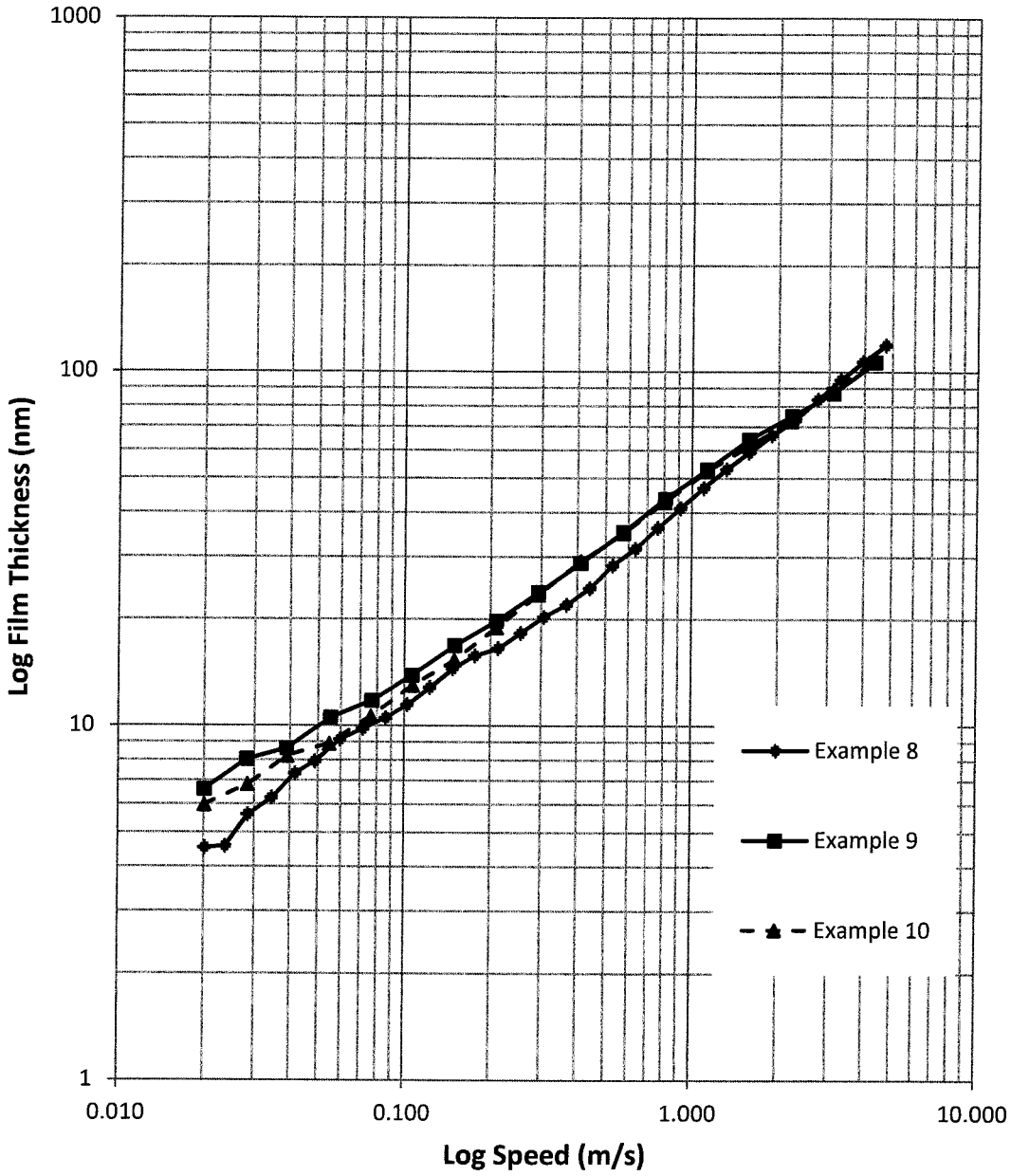

1000
100
10
1
Log Film Thickness (nm)
0.010
0.100
1.000
10.000
Log Speed (m/s)
Example 8
Example 9
Example 10

FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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