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TITLE

High Molecular Weight Amide/Ester Containing Quaternary Ammonium Salts

FIELD OF THE INVENTION

[0001] The present technology is related to amide or ester containing quaternary ammonium salts having a hydrocarbyl substituent of number average molecular weight (M_n) of 1300 to 3000, and the use of such quaternary ammonium salts in fuel and lubricant compositions to improve the water shedding performance of the composition. The invention further relates to a method of lubricating an internal combustion engine with the lubricant composition for at least one of antiwear, friction, detergency, dispersancy, and/or corrosion control performance.

BACKGROUND OF THE INVENTION

[0002] Deposit formation in diesel fuel injector nozzles is highly problematic, resulting in incomplete diesel combustion, and therefore power loss and misfiring. Traditionally polyisobutylene succinimide detergents have been used to inhibit injector fouling, but these materials have shown poor efficacy in modern engines. A new class of compounds based on quaternized polyisobutylene succinimides has been shown to provide improved detergency performance in both the traditional and modern diesel engines.

[0003] Although deposit control is the main function required of detergent molecules, there are a number of additional performance attributes which are desired. One of these is the ability of the detergent to shed water, or resolve water in oil emulsions. The entrainment of water in, for example, crude oil or downstream fuel pipelines, and during product transfer, can result in the formation of stable emulsions and suspended matter in the crude or fuel. Such emulsions can plug filters or otherwise make such emulsion containing fuels unacceptable. This could also result in corrosion issues downstream.

[0004] In order to assist in the water shedding process, a class of molecules known as demulsifiers can be added to fuel or crude oil formulations, whether in the pipeline, at the pump or as an aftermarket additive. While demulsifiers can assist in the water shedding process, it would be desirable to provide a new detergent molecule that provides improved demulsification or water shedding performance.

SUMMARY OF THE INVENTION

[0005] It has been found that quaternary ammonium salts prepared from hydrocarbyl substituted acylating agents, such as, for example, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n results in quaternary ammonium salts that, when blended into diesel fuel, provide improved demulsification performance compared to quaternary ammonium salts prepared from hydrocarbyl substituted acylating agents having a hydrocarbyl substituent with a number average molecular weight of around 1000 M_n . The number average molecular weight (M_n) may be measured using gel permeation chromatography (GPC) based on polystyrene standards.

[0006] Thus, in one aspect the present technology provides a composition including high M_n amide or ester containing quaternary ammonium salt (herein referred to as "high M_n amide/ester quat(s)"). The high M_n amide/ester quat itself can be the reaction product of (a) a quaternizable compound and (b) a quaternizing agent suitable for converting a quaternizable amino group of the nitrogen containing compound to a quaternary nitrogen. The quaternizable compound can be the reaction product of (i) a hydrocarbyl-substituted acylating agent, and (ii) a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with said hydrocarbyl-substituted acylating agent to form an ester or amide, and further having at least one quaternizable amino group. The hydrocarbyl-substituent can have a number average molecular weight, M_n , of greater than 1200, such as, for example, from 1300 to 3000.

[0007] In an embodiment, the quaternizable amino group can be a primary, secondary or tertiary amino group. In a further embodiment, the hydrocarbyl-substituted acylating agent can be polyisobutenyl succinic anhydride or polyisobutenyl succinic acid.

[0008] In some embodiments, the reaction to prepare the quaternizable compound of (a) can be carried out at a temperature of greater than 80 or 90 or 100 °C. In some embodiments, water produced during the condensation reaction, or water of reaction, can be removed. In some embodiments, the reaction to prepare the quaternizable compound of (a) can be carried out at a temperature of less than 80 °C. In yet another embodiment, the reaction can be carried out at 120 °C.

[0009] In an embodiment, the high M_n amide/ester quat is an amide containing quaternary ammonium salt. In another embodiment, the high M_n amide/ester quat is an

ester containing quaternary ammonium salt. In yet another embodiment, the high M_n amide/ester quat includes both amide and ester containing quaternary ammonium salts.

[0010] In other embodiments, the quaternizing agents can exclude methyl salicylate. In the same or different embodiments, the nitrogen containing compound can exclude dimethylaminopropylamine.

[0011] In still further embodiments, the quaternizing agent can be a dialkyl sulfate, an alkyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, a carboxylate, alkyl esters, or mixtures thereof. In some cases the quaternizing agent can be a hydrocarbyl epoxide. In some cases the quaternizing agent can be a hydrocarbyl epoxide in combination with an acid. In some cases the quaternizing agent can be an oxalate or terephthalate.

[0012] In some embodiments, the quaternizing agent can be employed in the presence of a protic solvent. In some embodiments, the quaternizing agent can be employed in the presence of 2-ethylhexanol, water, or mixtures thereof. In some embodiments, the quaternizing agent can be employed in the presence of an acid. In some embodiments, the quaternizing agent can be employed in the presence of an acid separate from the acid group present on the acylating agent. In some embodiments, the quaternizing agent can be employed in the presence of the acid group present in the structure of the acylating agent.

[0013] In some embodiments, the compositions described above can further include at least one other additive. In some instances, the at least one other additive can be a detergent, a demulsifier, a lubricating agent, a cold flow improver, an antioxidant, or a mixture thereof. In some instances the at least one other additive can be at least one non-quaternized hydrocarbyl-substituted succinic acid. In some instances, the at least one other additive can be at least one hydrocarbyl-substituted quaternary ammonium salt. In some instances where the at least one other additive is a non-quaternized or quaternized hydrocarbyl-substituted succinic acid, the hydrocarbyl-substituent can be a polyisobutylene having a molecular weight of 100 to 5000. In an embodiment, the at least one other additive can be at least one Mannich compound.

[0014] A further aspect of the present technology includes a composition having an amide or ester containing quaternary ammonium salt as described, and further having a fuel that is liquid at room temperature. In some embodiments the fuel can be a diesel fuel. A further aspect of the present technology includes a composition having an amide or ester

containing quaternary ammonium salt as described, and further having an oil of lubricating viscosity.

[0015] A still further aspect of the present technology provides a method of operating an internal combustion engine. In one embodiment, the method can include the steps of (a) supplying to the engine a fuel composition and (b) operating said engine. The fuel composition employed in the foregoing method can include (i) a fuel which is liquid at room temperature, and (ii) a composition comprising an amide or ester containing quaternary ammonium salt as described herein. In another embodiment, the method of operating an internal combustion engine can include the steps of (a) supplying a lubricating oil composition to the crankcase of the engine and (b) operating said engine. The lubricating oil composition can include (i) oil of lubricating viscosity, and (ii) the amide or ester containing quaternary ammonium salt as described herein.

[0016] Embodiments of the present technology may provide the use of the amide or ester containing quaternary ammonium salt for at least one of antiwear performance, friction modification (particularly for enhancing fuel economy), detergent performance (particularly deposit control or varnish control), dispersancy (particularly soot control or sludge control), or corrosion control. A particular embodiment of the present technology provides a method of improving water shedding performance, or demulsification, of a fuel composition. The method includes employing in a fuel which is liquid at room temperature a composition containing an amide or ester containing quaternary ammonium salt as described herein. Also provided is the use of a composition containing an amide or ester containing quaternary ammonium salt as described herein, to provide improved demulsification performance in a fuel that is liquid at room temperature.

[0017] In another embodiment, a composition comprising high number average molecular weight ester or amide containing quaternary ammonium salt ("high M_n amide/ester quat") is disclosed. The high M_n amide/ester quat may comprise the reaction product of a quaternizable compound and a quaternizing agent suitable for converting the quaternizable amino group of the nitrogen containing compound to a quaternary nitrogen. The quaternizable compound may be the reaction product of a hydrocarbyl-substituted acylating agent, wherein the hydrocarbyl-substituent has a number average molecular weight of 1300 to 3000, and a nitrogen containing compound having a nitrogen atom capable of reacting with the hydrocarbyl-substituted acylating agent to form an imide, and

further having at least one quaternizable amino group. The quaternizable amino group may be a primary, secondary or tertiary amino group.

[0018] In one embodiment, the hydrocarbyl-substituted acylating agent may be polyisobutenyl succinic anhydride or polyisobutenyl succinic acid. In yet another embodiment, the reaction of the hydrocarbyl-substituted acylating agent and the nitrogen containing compound may be carried out at a temperature of greater than 80 °C.

[0019] In one embodiment, the nitrogen containing compound excludes compounds comprising dimethylaminopropylamine.

[0020] In another embodiment, the quaternizing agent comprises at least one dialkyl sulfate, alkyl halide, hydrocarbyl substituted carbonate, hydrocarbyl epoxide, carboxylate, alkyl ester or mixtures thereof. In one embodiment, the quaternizing agent may be a hydrocarbyl epoxide. Alternatively, the quaternizing agent may be a hydrocarbyl epoxide in combination with an acid. In another embodiment, the quaternizing agent may be an oxalate or terephthalate. In yet another embodiment, the quaternizing agent excludes methyl salicylate.

[0021] The disclosed compositions comprising high M_n amide/ester quat may further comprise at least one other additive. Suitable additives include, but are not limited to, detergents, dispersants, demulsifiers, lubricity agents, cold flow improvers, antioxidants, or mixtures thereof.

[0022] In one embodiment, the at least one other additive comprises at least one hydrocarbyl-substituted succinic acid or at least one hydrocarbyl-substituted quaternary ammonium salt. The hydrocarbyl-substituent may be a polyisobutylene having a molecular weight ranging from 100 to 5000.

[0023] In another embodiment, the at least one other additive comprises at least one detergent/dispersant that is an amphiphilic substance which possess at least one hydrophobic hydrocarbon radical with a number average molecular weight of 100 to 10000 and at least one polar moiety selected from (i) Mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties; (ii) Hydroxyl groups in combination with mono or polyamino groups, at least one nitrogen atoms having basic properties; (v) Polyoxy-C₂ to C₄ alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups; (vii) Moieties derived from succinic anhydride and having hydroxyl and/or amino

and/or amido and/or imido groups; and/or (viii) Moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono-or polyamines. In yet another embodiment, the at least one other additive may comprise at least one Mannich compound.

5 [0024] In another embodiment, the disclosed compositions may further comprise a fuel that is liquid at room temperature. The fuel may be gasoline or diesel. The fuel composition may comprise at least one of a low number average molecular weight soap, a low number average molecular weight polyisobutylene succinimide (PIBSI), or a mixture thereof. The low molecular weight soap may have a number average molecular weight (M_n) of less than 340.

10 [0025] In yet another embodiment, the fuel composition may comprise 0.01 to 25 ppm of a metal and 1 to 12 ppm of a corrosion inhibitor. The corrosion inhibitor may be an alkenyl succinic acid comprising at least one of dodecenyl succinic acid (DDSA), hexadecenyl succinic acid (HDSA), or mixtures thereof.

15 [0026] In yet another embodiment, the fuel composition comprises PIBSI with a low number average molecular weight M_n of less than 400.

[0027] A method of improving water shedding performance of a gasoline or diesel fuel composition is also disclosed. The method may comprise employing a composition comprising high M_n amide/ester quat as described above. The high M_n amide/ester quat may be added to the fuel in an amount ranging from 5 to 1000 ppm by weight based on a total weight of the fuel composition.

20 [0028] In yet another method, the composition comprising a high M_n amide/ester quat may further comprise an oil of lubricating viscosity.

[0029] A method of operating an internal combustion engine is also disclosed. The method may comprise supplying a fuel which is liquid at room temperature having a composition comprising a high M_n amide/ester quat therein to the engine and operating the engine. The high M_n amide/ester quat may be added to the fuel in an amount ranging from 5 to 1000 ppm by weight based on a total weight of the fuel composition.

25 [0030] In yet another embodiment, the method of operating an internal combustion engine may comprise supplying an oil of lubricating viscosity having a composition comprising a high M_n amide/ester quat therein to the engine crankcase and operating the engine. The high M_n amide/ester quat may be added to the oil on an active basis 1-5 wt%.

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The oil of lubricating viscosity may have a total sulfated ash of less than 1 wt% and/or a phosphorus content of less than 0.11 wt%.

[0031] A method of reducing and/or preventing injector deposits is also disclosed. The method may comprise supplying a fuel composition having a composition comprising a high M_n amide/ester quat therein to a fuel injector of the engine and operating the engine. The deposits may be internal diesel injector deposits (IDID). In yet another embodiment, the deposits may comprise a low number average molecular weight soap, a low number average molecular weight polyisobutylene succinimide (PIBSI), or mixtures thereof.

[0032] In another embodiment, the fuel may comprise a molecular weight soap with a number average molecular weight (M_n) of less than 340.

[0033] In another embodiment, the fuel may comprise 0.01 to 25 ppm of a metal and 1 to 12 ppm of a corrosion inhibitor. In yet another embodiment, the corrosion inhibitor may be an alkenyl succinic acid comprising at least one of dodecenyl succinic acid (DDSA), hexadecenyl succinic acid (HDSA), or mixtures thereof.

[0034] In another embodiment, the fuel comprises a PIBSI with a low number average molecular weight M_n of less than 400. The fuel may be gasoline or diesel. In yet another embodiment, the engine may comprise a high pressure common rail injector system.

[0035] The use of a composition comprising a high M_n amide/ester quat to reduce and/or prevent internal deposits in an engine operated with a gasoline or diesel fuel is also disclosed. In one embodiment, the engine may comprise a high pressure common rail injector system. In yet another embodiment, the high M_n amide/ester quat may be used to reduce and/or prevent internal diesel injector deposits (IDID).

DETAILED DESCRIPTION OF THE INVENTION

[0036] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0037] One aspect of the current technology relates to a composition of an amide or ester containing quaternary ammonium salt (high M_n amide/ester quat).

[0038] The number average molecular weight of the materials described herein is measured using gas permeation chromatography (GPC) using a Waters GPC 2000 equipped with a refractive index detector and Waters EmpowerTM data acquisition and analysis software. The columns are polystyrene (PLgel, 5 micron, available from Agilent/Polymer Laboratories, Inc.). For the mobile phase, individual samples are

dissolved in tetrahydrofuran and filtered with PTFE filters before they are injected into the GPC port.

Waters GPC 2000 Operating Conditions:

Injector, Column, and Pump/Solvent compartment temperatures: 40° C

5 Autosampler Control: Run time: 40 minutes

Injection volume: 300 microliter

Pump: System pressure: ~90 bars (Max. pressure limit: 270 bars, Min. pressure limit: 0 psi)

Flow rate: 1.0 ml/minute

10 Differential Refractometer (RI): Sensitivity: -16; Scale factor: 6

High M_n Amide/Ester Quats

[0039] The production of a quaternary ammonium salt generally results in a mixture of compounds including a quaternary ammonium salt or salts, and this mixture may be difficult to define apart from the process steps employed to produce the quaternary ammonium salt. Further, the process by which a quaternary ammonium salt is produced can be influential in imparting distinctive structural characteristics to the final quaternary ammonium salt product that can affect the properties of the quaternary ammonium salt product. Thus, in one embodiment, the amide or ester containing quaternary ammonium salts of the present technology may be described as a reaction product of (a) a quaternizable compound, and (b) a quaternizing agent. As used herein, reference to high M_n amide/ester quat(s) includes reference to the mixture compounds including a quaternary ammonium salt or salts as described herein, as well as referring to the quaternary ammonium salt itself.

[0040] The quaternizable compound of (a) employed to prepare the high M_n amide/ester quat itself may be the reaction product of (i) a hydrocarbyl-substituted acylating agent, and (ii) a nitrogen containing compound. More particularly, the hydrocarbyl-substituted acylating agent of (a)(i) can be an acylating agent functionalized with a hydrocarbyl-substituent having a number average molecular weight of 1300 to 3000.

[0041] Examples of quaternary ammonium salts and methods for preparing the same are described in the following patents, which are hereby incorporated by reference, US

4,253,980, US 3,778,371, US 4,171,959, US 4,326,973, US 4,338,206, US 5,254,138, and US 7,951,211.

[0042] Details regarding the quaternizable compound, and specifically, the hydrocarbyl-substituted acylating agent and the nitrogen containing compound, as well as the quaternizing agent, are provided below.

The Hydrocarbyl Substituted Acylating Agent

[0043] The hydrocarbyl substituted acylating agent employed to prepare the quaternizable compound can be the reaction product of the precursor to the hydrocarbyl-substituent, which is a long chain hydrocarbon, generally a polyolefin, with a monounsaturated carboxylic acid reactant such as (i) α,β -monounsaturated C₄ to C₁₀ dicarboxylic acid such as fumaric acid, itaconic acid, maleic acid.; (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or di-esters of (i); (iii) α,β -monounsaturated C₃ to C₁₀ monocarboxylic acid such as acrylic acid and methacrylic acid.; or (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived esters of (iii).

[0044] The hydrocarbyl-substituent is a long chain hydrocarbyl group. In one embodiment, the hydrocarbyl group can have a number average molecular weight (M_n) of 1300 to 3000. The M_n of the hydrocarbyl-substituent can also be from 1500 to 2800 or 2900, or from 1700 to 2700, or from 1900 to 2600, or 2000 to 2500. In an embodiment, the hydrocarbyl-substituent can be any compound containing an olefinic bond represented by the general formula:



wherein each of R¹ and R² is, independently, hydrogen or a hydrocarbon based group. Each of R⁶, R⁷ and R⁸ is, independently, hydrogen or a hydrocarbon based group; preferably at least one is a hydrocarbon based group containing at least 20 carbon atoms.

[0045] Olefin polymers for reaction with the monounsaturated carboxylic acids can include polymers comprising a major molar amount of C₂ to C₂₀, e.g. C₂ to C₅ monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, or styrene. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of; ethylene and propylene; butylene and isobutylene; propylene and isobutylene. Other copolymers include those in

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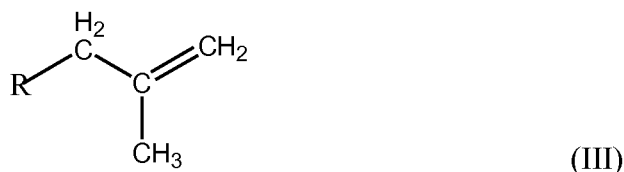
which a minor molar amount of the copolymer monomers e.g., 1 to 10 mole % is a C₄ to C₁₈ diolefin, e.g., a copolymer of isobutylene and butadiene; or a copolymer of ethylene, propylene and 1,4-hexadiene.

[0046] In one embodiment, at least one R of formula (I) is derived from polybutene, that is, polymers of C₄ olefins, including 1-butene, 2-butene and isobutylene. C₄ polymers can include polyisobutylene. In another embodiment, at least one R of formula (I) is derived from ethylene- α olefin polymers, including ethylene-propylene-diene polymers. Ethylene- α olefin copolymers and ethylene-lower olefin-diene terpolymers are described in numerous patent documents, including European patent publication EP 0 279 863 and the following United States patents: 3,598,738; 4,026,809; 4,032,700; 4,137,185; 4,156,061; 4,320,019; 4,357,250; 4,658,078; 4,668,834; 4,937,299; 5,324,800 each of which are incorporated herein by reference for relevant disclosures of these ethylene based polymers.

[0047] In another embodiment, the olefinic bonds of formula (I) are predominantly vinylidene groups, represented by the following formulas:



wherein R is a hydrocarbyl group



wherein R is a hydrocarbyl group.

[0048] In one embodiment, the vinylidene content of formula (I) can comprise at least 30 mole % vinylidene groups, at least 50 mole % vinylidene groups, or at least 70 mole % vinylidene groups. Such material and methods for preparing them are described in U.S. Pat. Nos. 5,071,919; 5,137,978; 5,137,980; 5,286,823, 5,408,018, 6,562,913, 6,683,138, 7,037,999 and U.S. Publication Nos. 20040176552A1, 20050137363 and 20060079652A1, which are expressly incorporated herein by reference, such products are

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commercially available by BASF, under the trade name GLISSOPAL® and by Texas PetroChemical LP, under the trade name TPC 1105™ and TPC 595™.

[0049] In other embodiments, the hydrocarbyl-substituted acylating agent may be a “conventional” vinylidene polyisobutylene (PIB) wherein less than 20% of the head groups are vinylidene head groups as measured by nuclear magnetic resonance (NMR). Alternatively, the hydrocarbyl-substituted acylating agent may be a mid-vinylidene PIB or a high-vinylidene PIB. In mid-vinylidene PIBs, the percentage of head groups that are vinylidene groups can range from greater than 20% to 70%. In high-vinylidene PIBs, the percentage of head groups that are vinylidene head groups is greater than 70%.

[0050] Methods of making hydrocarbyl substituted acylating agents from the reaction of the monounsaturated carboxylic acid reactant and the compound of formula (I) are well known in the art and disclosed in the following patents: U.S. Pat. Nos. 3,361,673 and 3,401,118 to cause a thermal “ene” reaction to take place; U.S. Pat. Nos. 3,087,436; 3,172,892; 3,272,746, 3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; 6,077,909; 6,165,235 and are hereby incorporated by reference.

[0051] The hydrocarbyl substituted acylating agent may also be a copolymer formed by copolymerizing at least one monomer that is an ethylenically unsaturated hydrocarbon having 2 to 100 carbon atoms. The monomer may be linear, branched, or cyclic. The monomer may have oxygen or nitrogen substituents, but will not react with amines or alcohols. The monomer may be reacted with a second monomer that is a carboxylic acid or carboxylic acid derivative having 3 to 12 carbon atoms. The second monomer may have one or two carboxylic acid functional groups and is reactive with amines or alcohols. When made using this process, the hydrocarbyl substituted acylating agent copolymer has a number average molecular weight Mn of 500 to 20,000.

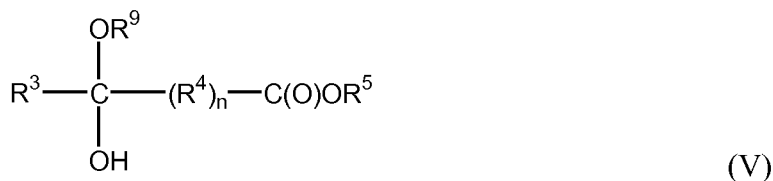
[0052] Alternatively, the hydrocarbyl substituted acylating agent may be a terpolymer that is the reaction product of ethylene and at least one monomer that is an ethylenically unsaturated monomer having at least one tertiary nitrogen atom, with (i) an alkenyl ester of one or more aliphatic monocarboxylic acids having 1 to 24 carbon atoms or (ii) an alkyl ester of acrylic or methacrylic acid.

[0053] In another embodiment, the hydrocarbyl substituted acylating agent can be made from the reaction of at least one carboxylic reactant represented by the following formulas:

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and



wherein each of R^3 , R^5 and R^9 is independently H or a hydrocarbyl group, R^4 is a divalent hydrocarbylene group and n is 0 or 1 with any compound containing an olefin bond as represented by formula (I). Compounds and the processes for making these compounds are disclosed in U.S. Pat. Nos. 5,739,356; 5,777,142; 5,786,490; 5,856,524; 6,020,500; and 6,114,547.

[0054] In yet another embodiment, the hydrocarbyl substituted acylating agent can be made from the reaction of any compound represented by formula (I) with (IV) or (V), and can be carried out in the presence of at least one aldehyde or ketone. Suitable aldehydes include formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, pentanal, hexanal, heptaldehyde, octanal, benzaldehyde, and higher aldehydes. Other aldehydes, including monoaldehydes, and dialdehydes, such as glyoxal, may also be used. In one embodiment, aldehyde is formaldehyde, which can be supplied as the aqueous solution often referred to as formalin, but is more often used in the polymeric form as paraformaldehyde, which is a reactive equivalent of, or a source of, formaldehyde. Other reactive equivalents include hydrates or cyclic trimers. Suitable ketones include acetone, butanone, methyl ethyl ketone, and other ketones. In one embodiment of the disclosed technology, one of the two hydrocarbyl groups is methyl. Mixtures of two or more aldehydes and/or ketones are also useful. Compounds and the processes for making these compounds are disclosed in U.S. Pat. Nos. 5,840,920; 6,147,036; and 6,207,839.

[0055] In another embodiment, the hydrocarbyl substituted acylating agent can include, methylene bis-phenol alkanoic acid compounds, the condensation product of (i) aromatic compound of the formula:



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wherein R is independently a hydrocarbyl group, Ar is an aromatic group containing from 5 to 30 carbon atoms and from 0 to 3 optional substituents such as amino, hydroxy- or alkyl- polyoxyalkyl, nitro, aminoalkyl, carboxy or combinations of two or more of said optional substituents, Z is independently OH, lower alkoxy, $(OR^{10})_bOR^{11}$, or O- wherein each R^{10} is independently a divalent hydrocarbyl group, R^{11} is H or hydrocarbyl and b is a number ranging from 1 to 30, c is a number ranging from 1 to 3 and m is 0 or an integer from 1 up to 6 with the proviso that m does not exceed the number of valences of the corresponding Ar available for substitution and (ii) at least on carboxylic reactant such as the compounds of formula (IV) and (V) described above. In one embodiment, at least one hydrocarbyl group on the aromatic moiety is derived from polybutene. In one embodiment, the source of hydrocarbyl groups are above described polybutenes obtained by polymerization of isobutylene in the presence of a Lewis acid catalyst such as aluminum trichloride or boron trifluoride. Compounds and the processes for making these compounds are disclosed in U.S. Pat. Nos. 3,954,808; 5,336,278; 5,458,793; 5,620,949; 5,827,805; and 6,001,781.

[0056] In another embodiment, the reaction of (i) with (ii), optionally in the presence of an acidic catalyst such as organic sulfonic acids, heteropolyacids, and mineral acids, can be carried out in the presence of at least one aldehyde or ketone. The aldehyde or ketone reactant employed in this embodiment is the same as those described above. The ratio of the hydroxyaromatic compound: carboxylic reactant:aldehyde or ketone can be 2:(0.1 to 1.5): (1.9 to 0.5). In one embodiment, the ratio is 2:(0.8 to 1.1): (1.2 to 0.9). The amounts of the materials fed to the reaction mixture will normally approximate these ratios, although corrections may need to be made to compensate for greater or lesser reactivity of one component or another, in order to arrive at a reaction product with the desired ratio of monomers. Such corrections will be apparent to the person skilled in the art. While the three reactants can be condensed simultaneously to form the product, it is also possible to conduct the reaction sequentially, whereby the hydroxyaromatic is reacted first with either the carboxylic reactant and thereafter with the aldehyde or ketone, or vice versa. Compounds and the processes for making these compounds are disclosed in U.S. Pat. No. 5,620,949.

[0057] In yet another embodiment the hydrocarbyl substituted acylating agent can include a mono-, dimer or trimer carboxylic acid with 8 to 54 carbon atoms and is reactive

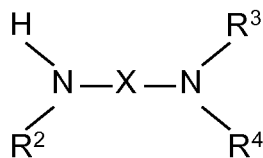
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with primary or secondary amines. Suitable acids include, but are not limited to, the mono-, dimer, or trimer acids of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic, arachidic acid, behenic acid, lignoceric acid, cerotic acid, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, α -linolenic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, and docosahexaenoic acid. Other methods of making the hydrocarbyl substituted acylating agent can be found in the following reference, U.S. Pat. Nos. 5,912,213; 5,851,966; and 5,885,944 which are hereby incorporated by reference.

Nitrogen Containing Compound

[0058] The composition of the present invention contains a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with the acylating agent and further having a quaternizable amino group. A quaternizable amino group is any primary, secondary or tertiary amino group on the nitrogen containing compound that is available to react with a quaternizing agent to become a quaternary amino group.

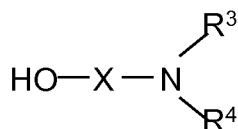
[0059] In one embodiment, the nitrogen containing compound can be represented by the following formulas:



(VII)

wherein X is an alkylene group containing 1 to 4 carbon atoms; R^2 is hydrogen or a hydrocarbyl group; and R^3 and R^4 are hydrocarbyl groups;

or



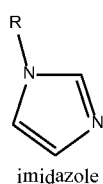
(VIII)

wherein X is a alkylene group containing about 1 to about 4 carbon atoms; R^3 and R^4 are hydrocarbyl groups.

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[0060] Examples of the nitrogen containing compound capable of reacting with the acylating agent can include, but are not limited to, dimethylaminopropylamine, N,N-dimethyl-aminopropylamine, N,N-diethyl-aminopropylamine, N,N-dimethyl-aminoethylamine ethylenediamine, 1,2-propylenediamine, 1,3-propylene diamine, the isomeric butylenediamines, pentanediamines, hexanediamines, heptanediamines, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, hexamethylenetetramine, and bis(hexamethylene) triamine, the diaminobenzenes, the diaminopyridines or mixtures thereof. The nitrogen containing compounds capable of reacting with the acylating agent and further having a quaternizable amino group can further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, 3'3'-iminobis(N,N-dimethylpropylamine). Additional nitrogen containing compounds capable of reacting with the acylating agent and having a quaternizable amino group include alkanolamines including but not limited to triethanolamine, trimethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, N,N,N-tris(hydroxyethyl)amine, N,N,N-tris(hydroxymethyl)amine, N,N-dimethylethanolamine, N,N-diethylethanolamine, 2-(diisopropylamino)ethanol, 2-(dibutylamino)ethanol, 3-dimethylamino-1-propanol, 3-diethylamino-1-propanol, 1-dimethylamino-2-propanol, 1-diethylamino-2-propanol, 2-dimethylamino-2-methyl-1-propanol, 5-dimethylamino-2-propanol, 2-[2-(dimethylamino)ethoxy]-ethanol, 4-methyl-2-(piperidino methyl)phenol, 1-benzyl-3-pyrrolidinol, 1-benzylpyrrolidine-2-methanol, 2,4,6-tri(dimethylaminomethyl)phenol, dialkoxylated amines such as Ethermeen T12. In some embodiments, the nitrogen containing compound excludes dimethylaminopropylamine.

[0061] In one embodiment, the nitrogen containing compound can be an imidazole, for example, as represented by the following formula:



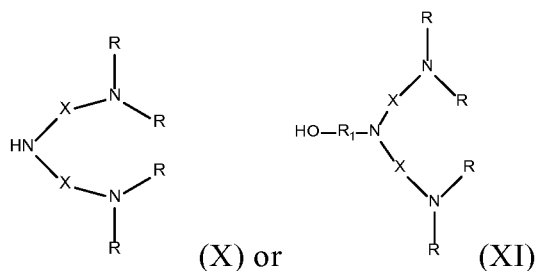
imidazole

(IX)

-16-

wherein R is an amine or alkanol capable of condensing with said hydrocarbyl-substituted acylating agent and having from 3 to 8 carbon atoms.

[0062] In one embodiment, the nitrogen containing compound can be represented by at least one of formulas X or XI:



wherein each X can be, individually, a C1 to C6 hydrocarbylene group, and each R can be, individually, a hydrogen or a C1 to C6 hydrocarbyl group. In one embodiment, X can be, for example, a C1, C2 or C3 alkylene group. In the same or different embodiments, each R can be, for example, H or a C1, C2 or C3 alkyl group.

Quaternizable Compound

[0063] The hydrocarbyl substituted acylating agents and nitrogen containing compounds described above are reacted together to form a quaternizable compound. Methods and process for reacting the hydrocarbyl substituted acylating agents and nitrogen containing compounds are well known in the art.

[0064] In embodiments, the reaction between the hydrocarbyl substituted acylating agents and nitrogen containing compounds can be carried out at temperatures of greater than about 80 °C, or 90 °C, or in some cases 100 °C, such as between 100 and 150 or 200 °C, or 125 and 175 °C. At the foregoing temperatures water may be produced during the condensation, which is referred to herein as the water of reaction. In some embodiments, the water of reaction can be removed during the reaction, such that the water of reaction does not return to the reaction and further react. The hydrocarbyl substituted acylating agents and nitrogen containing compounds may be reacted at a ratio of 1:1, but the reaction may also contain the respective reactants (i.e., hydrocarbyl substituted acylating agent:nitrogen containing compound) in ratios from 3:1 to 1:1.2, or from 2.5:1 to 1:1.1, and in some embodiments from 2:1 to 1:1.05.

Quaternizing agent

[0065] The quaternary ammonium salt can be formed when the quaternizable compound, that is, the reaction products of the hydrocarbyl substituted acylating agent and nitrogen containing compounds described above, are reacted with a quaternizing agent.

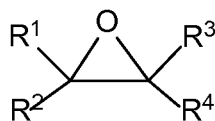
5 Suitable quaternizing agents can include, for example, dialkyl sulfates, alkyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides, carboxylates, alkyl esters, and mixtures thereof.

[0066] In one embodiment, the quaternizing agent can include alkyl halides, such as chlorides, iodides or bromides; alkyl sulfonates; dialkyl sulfates, such as, dimethyl sulfate and diethyl sulfate; sultones; alkyl phosphates; such as, C1-12 trialkylphosphates; di C1-12 alkylphosphates; borates; C1-12 alkyl borates; alkyl nitrites; alkyl nitrates; dialkyl carbonates, such as dimethyl oxalate; alkyl alkanoates, such as methyl salicylate; O,O-di-C1-12 alkyldithiophosphates; or mixtures thereof.

[0067] In one embodiment, the quaternizing agent may be derived from dialkyl sulfates such as dimethyl sulfate or diethyl sulfate, N-oxides, sultones such as propane and butane sultone; alkyl, acyl or aryl halides such as methyl and ethyl chloride, bromide or iodide or benzyl chloride, and a hydrocarbyl (or alkyl) substituted carbonates. If the alkyl halide is benzyl chloride, the aromatic ring is optionally further substituted with alkyl or alkenyl groups.

20 [0068] The hydrocarbyl (or alkyl) groups of the hydrocarbyl substituted carbonates may contain 1 to 50, 1 to 20, 1 to 10 or 1 to 5 carbon atoms per group. In one embodiment, the hydrocarbyl substituted carbonates contain two hydrocarbyl groups that may be the same or different. Examples of suitable hydrocarbyl substituted carbonates include dimethyl or diethyl carbonate.

25 [0069] In another embodiment, the quaternizing agent can be a hydrocarbyl epoxide, for example, as represented by the following formula:



(XII)

wherein R^1 , R^2 , R^3 and R^4 can be independently H or a hydrocarbyl group contain from 1 to 50 carbon atoms. Examples of hydrocarbyl epoxides include: ethylene oxide, propylene oxide, butylene oxide, styrene oxide and combinations thereof. In one embodiment the quaternizing agent does not contain any styrene oxide.

5 [0070] In some embodiments, the hydrocarbyl epoxide can be an alcohol functionalized epoxide, C_4 to C_{14} epoxides, and mixtures thereof. In another embodiment, the epoxide may be a C_4 to C_{20} epoxide.

10 [0071] Exemplary C_4 to C_{14} epoxides are those of formula XII where R^1 , R^2 , R^3 and R^4 can be independently H or a C_2 to C_{12} hydrocarbyl group. In an embodiment, the epoxides can be C_4 to C_{14} epoxides. Epoxides suitable as quaternizing agents in the present technology can include, for example, C_4 to C_{14} epoxides having linear hydrocarbyl substituents, such as, for example, 2-ethyloxirane, 2-propyloxirane, and the like, and C_4 to C_{14} epoxides having branched and cyclic or aromatic substituents, such as, for example, styrene oxide. C_4 to C_{14} epoxides can also include epoxidized tri-glycerides, fats or oils; 15 epoxidized alkyl esters of fatty acids; and mixtures thereof.

[0072] Exemplary alcohol functionalized epoxides can include those of formula XII where R^1 , R^2 , R^3 and R^4 can be independently H or a hydroxyl containing hydrocarbyl group. In an embodiment, hydroxyl containing hydrocarbyl group can contain from 2 to 32, or from 3 to 28, or even from 3 to 24 carbon atoms. Exemplary alcohol functionalized 20 epoxide derivatives can include for example, glycidol and the like.

[0073] In some embodiments the hydrocarbyl epoxide can be employed in combination with an acid. The acid used with the hydrocarbyl epoxide may be a separate component, such as acetic acid. In other embodiments, a small amount of an acid component may be present, but at <0.2 or even <0.1 moles of acid per mole of hydrocarbyl 25 acylating agent. These acids may also be used with the other quaternizing agents described above, including the hydrocarbyl substituted carbonates and related materials described below.

[0074] In some embodiments the quaternizing agent does not contain any substituent group that contains more than 20 carbon atoms.

30 [0075] In another embodiment the quaternizing agent can be an ester of a carboxylic acid capable of reacting with a tertiary amine to form a quaternary ammonium salt, or an

ester of a polycarboxylic acid. In a general sense such materials may be described as compounds having the structure:



where R^{19} is an optionally substituted alkyl, alkenyl, aryl or alkylaryl group and R^{20} is a hydrocarbonyl group containing from 1 to 22 carbon atoms.

[0076] Suitable compounds include esters of carboxylic acids having a pKa of 3.5 or less. In some embodiments the compound is an ester of a carboxylic acid selected from a substituted aromatic carboxylic acid, an α -hydroxycarboxylic acid and a polycarboxylic acid. In some embodiments the compound is an ester of a substituted aromatic carboxylic acid and thus R^{19} is a substituted aryl group. R^{19} may be a substituted aryl group having 6 to 10 carbon atoms, a phenyl group, or a naphthyl group. R^{19} may be suitably substituted with one or more groups selected from carboalkoxy, nitro, cyano, hydroxy, SR' or $NR'R''$ where each of R' and R'' may independently be hydrogen, or an optionally substituted alkyl, alkenyl, aryl or carboalkoxy groups. In some embodiments R' and R'' are each independently hydrogen or an optionally substituted alkyl group containing from 1 to 22, 1 to 16, 1 to 10, or even 1 to 4 carbon atoms.

[0077] In some embodiments R^{19} in the formula above is an aryl group substituted with one or more groups selected from hydroxyl, carboalkoxy, nitro, cyano and NH^2 . R^{19} may be a poly-substituted aryl group, for example trihydroxyphenyl, but may also be a mono-substituted aryl group, for example an ortho substituted aryl group. R^{19} may be substituted with a group selected from OH, NH_2 , NO_2 , or COOMe. Suitably R^{19} is a hydroxy substituted aryl group. In some embodiments R^{19} is a 2-hydroxyphenyl group. R^{20} may be an alkyl or alkylaryl group, for example an alkyl or alkylaryl group containing from 1 to 16 carbon atoms, or from 1 to 10, or 1 to 8 carbon atoms. R^{20} may be methyl, ethyl, propyl, butyl, pentyl, benzyl or an isomer thereof. In some embodiments R^{20} is benzyl or methyl. In some embodiments the quaternizing agent is methyl salicylate. In some embodiments the quaternizing agent excludes methyl salicylate.

[0078] In some embodiments the quaternizing agent is an ester of an α -hydroxycarboxylic acid. Compounds of this type suitable for use herein are described in EP 1254889. Examples of suitable compounds which contain the residue of an α -

hydroxycarboxylic acid include (i) methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of 2-hydroxyisobutyric acid; (ii) methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of 2-hydroxy-2-methylbutyric acid; (iii) methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of 2-hydroxy-2-ethylbutyric acid; (iv) methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of lactic acid; and (v) methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, allyl-, benzyl-, and phenyl esters of glycolic acid. In some embodiments the quaternizing agent comprises methyl 2-hydroxyisobutyrate.

[0079] In some embodiments the quaternizing agent comprises an ester of a polycarboxylic acid, including dicarboxylic acids and carboxylic acids having more than 2 acidic moieties. In some embodiments the esters are alkyl esters with alkyl groups that contain from 1 to 4 carbon atoms. Suitable examples include diesters of oxalic acid, diesters of phthalic acid, diesters of maleic acid, diesters of malonic acid or diesters or triesters of citric acid.

[0080] In some embodiments the quaternizing agent is an ester of a carboxylic acid having a pKa of less than 3.5. In such embodiments in which the compound includes more than one acid group, we mean to refer to the first dissociation constant. The quaternizing agent may be selected from an ester of a carboxylic acid selected from one or more of oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic acid, citric acid, nitrobenzoic acid, aminobenzoic acid and 2, 4, 6-trihydroxybenzoic acid. In some embodiments the quaternizing agent includes dimethyl oxalate, a terephthalate, such as dimethyl terephthalate, and methyl 2-nitrobenzoate.

[0081] Quaternizing agents capable of coupling more than one quaternizable compound also may be employed. By “coupling” more than one quaternizable compounds, it is meant that at least two quaternizable compounds react with the same quaternizing agent to form a compound of the at least two quaternizable compounds linked by the quaternizing agent. Such quaternizing agents may, in some instances, also be referred to as coupling quaternizing agents herein and can include, for example, polyepoxides, such as, for example, di-, tri-, or higher epoxides; polyhalides; epoxy-halides, aromatic polyesters, and mixtures thereof.

[0082] In one embodiment, the quaternizing agent can be a polyepoxide. Polyepoxides can include, for example, poly-glycidyls which can include, for example, di-

epoxyoctane; ethylene glycol diglycidyl ether; neopentyl glycol diglycidyl ether; 1,4-butanediol diglycidyl ether; 3(bis(glycidyl oxymethyl)-methoxy)-1,2-propanediol; 1,4-cyclohexane dimethanol diglycidyl ether; diepoxycyclo-octane, bisphenol A diglycidyl ether 4-vinyl-1-cyclohexene diepoxide; N,N-Diglycidyl-4-4glycidylxyaniline; 1,6-hexane diglycidyl ether; trimethylolpropanetriglycidyl ether; polypropyleneglycol diglycidyl ether; polyepoxidized tri-glycerides, fats or oils; and mixtures thereof.

[0083] In one embodiment, the quaternizing agent may be derived from polyhalides, such as, for example, chlorides, iodides or bromides. Such polyhalides can include, but not be limited to, 1,5-dibromopentane; 1,4-diiodobutane; 1,5-dichloropentane; 1,12-dichlorododecane; 1,12-dibromododecane; 1,2-diiodoethane; 1,2-dibromoethane; and mixtures thereof.

[0084] In an embodiment, the quaternizing agent can be an epoxy-halide, such as, for example, epichlorohydrin and the like.

[0085] The quaternizing agent may also be a poly aromatic ester. Examples of poly aromatic esters can include, but not be limited to, 4,4'-oxybis(methylbenzoate); dimethylterephthalate; and mixtures thereof.

[0086] In certain embodiments the molar ratio of the quaternizable compound to quaternizing agent is 1:0.1 to 2, or 1:1 to 1.5, or 1:1 to 1.3. In some embodiments, particularly when employing a coupling quaternizing agent, the ratio of the quaternizable compound to the quaternizing agent can be from 2:1 to 1:1.

[0087] Any of the quaternizing agents described above, including the hydrocarbyl epoxides, may be used in combination with an acid. Suitable acids include carboxylic acids, such as acetic acid, propionic acid, 2-ethylhexanoic acid, and the like.

[0088] In some embodiments, the quaternizing agent can be employed in the presence of a protic solvent, such as, for example, 2-ethylhexanol, water, and combinations thereof. In some embodiments, the quaternizing agent can be employed in the presence of an acid. In yet another embodiment, the quaternizing agent can be employed in the presence of an acid and a protic solvent. In some embodiments, the acid can be an acid component in addition to the acid group present in the structure of the acylating agent. In further embodiments the reaction can be free of, or essentially free of, any additional acid component other than the acid group present in the structure of the acylating agent. By "free of" it is meant completely free, and by "essentially free" it is meant an amount that

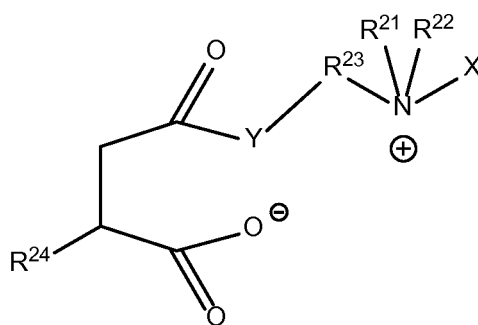
-22-

not materially affect the essential or basic and novel characteristics of the composition, such as, for example, less than 1% by weight.

Structure

[0089] While the process to prepare the quaternary ammonium salts can produce a mixture that is not readily definable apart from the process steps, certain structural components may be expected in some circumstances.

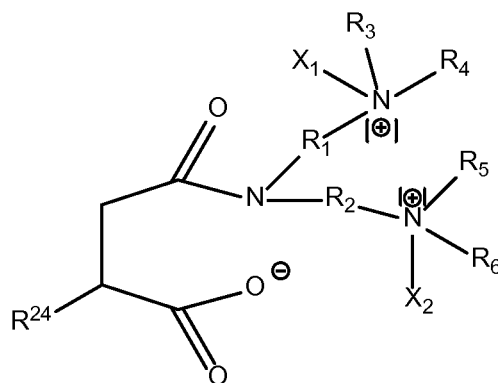
[0090] In some embodiments the quaternary ammonium salt can comprise, consist essentially of, or consist of a cation represented by the following formula:



(XV)

wherein: R^{21} and R^{22} are hydrocarbyl groups containing from 1 to 10 carbon atoms; R^{23} is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^{24} is a hydrocarbyl group containing from 92 to 215 carbon atoms, or from 107 to 200 or 210 carbon atoms, or from 120 to 195 carbon atoms, or from 135 to 190 or from 140 to 180 or 185 carbon atoms; X is a group derived from the quaternizing agent; and Y is oxygen or nitrogen.

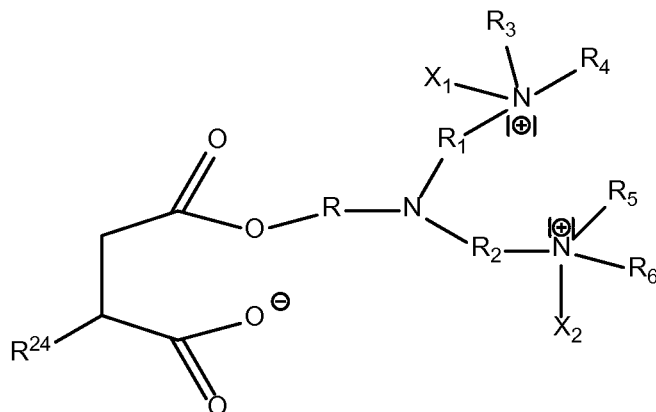
[0091] In some embodiments the quaternary ammonium salt can comprise, consist essentially of, or consist of a cation represented by the following formulas:



(XVI)

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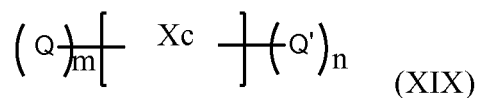
or



(XVII)

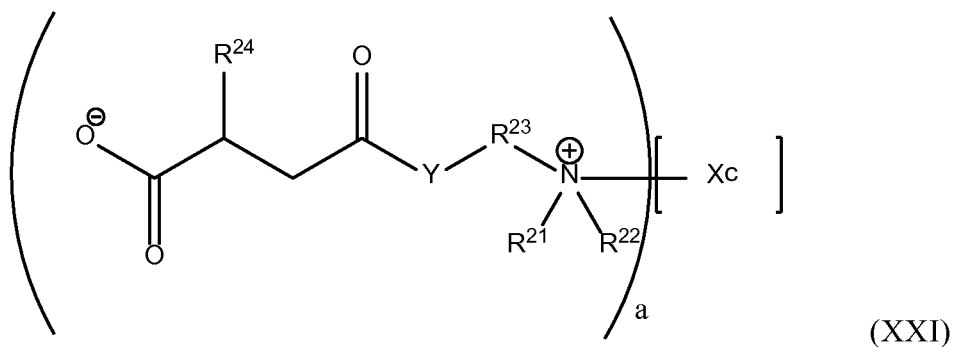
wherein: R can be a C1 to C6 alkyl group; R1 and R2, individually, can be a C1 to C6 hydrocarbyl group, for example a C1, C2, or C3 alkyl group; R3, R4, R5 and R6, individual, can be hydrogen or a C1 to C6 hydrocarbyl group, such as, for example, a C1, C2, or C3 alkyl group; R²⁴ is a hydrocarbyl group containing from 92 to 215 carbon atoms, or from 107 to 200 or 210 carbon atoms, or from 120 to 195 carbon atoms, or from 135 to 190 or from 140 to 180 or 185 carbon atoms; X1 and X2, individually, can be H or a group derived from the quaternizing agent, so long as at least one of X1 and X2 is a group derived from the quaternizing agent.

[0092] In some embodiments the quaternary ammonium salt can comprise, consist essentially of, or consist of a coupled quaternary ammonium compound represented by the following formula:

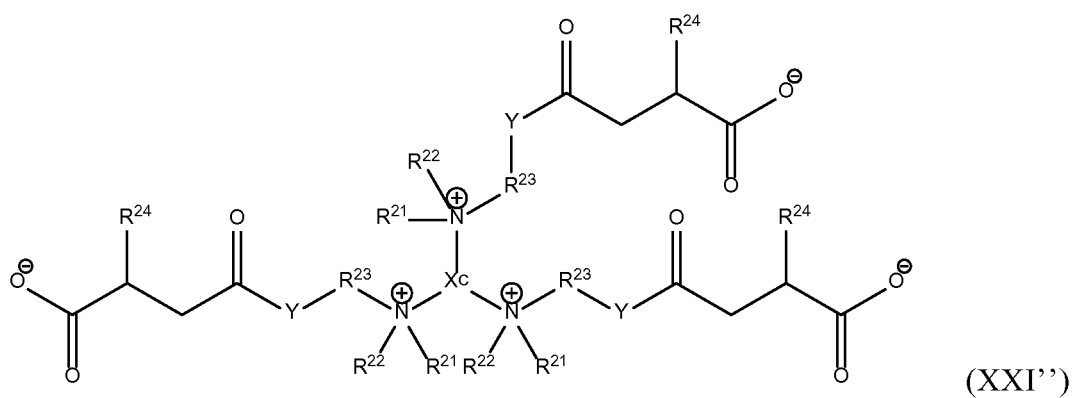
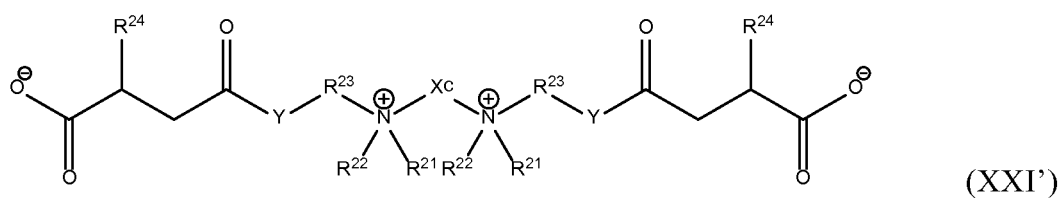


wherein: Q and Q' are the same or different and represent quaternizable compounds, m and n are, individually, integers of between 1 and 4, and Xc represents a group derived from a coupling quaternizing agent, such as, for example, 1,4-butanediol diglycidyl ether, or bisphenol A diglycidyl ether. Example coupled quaternary ammonium compounds can include, for example, any of the formulas below:

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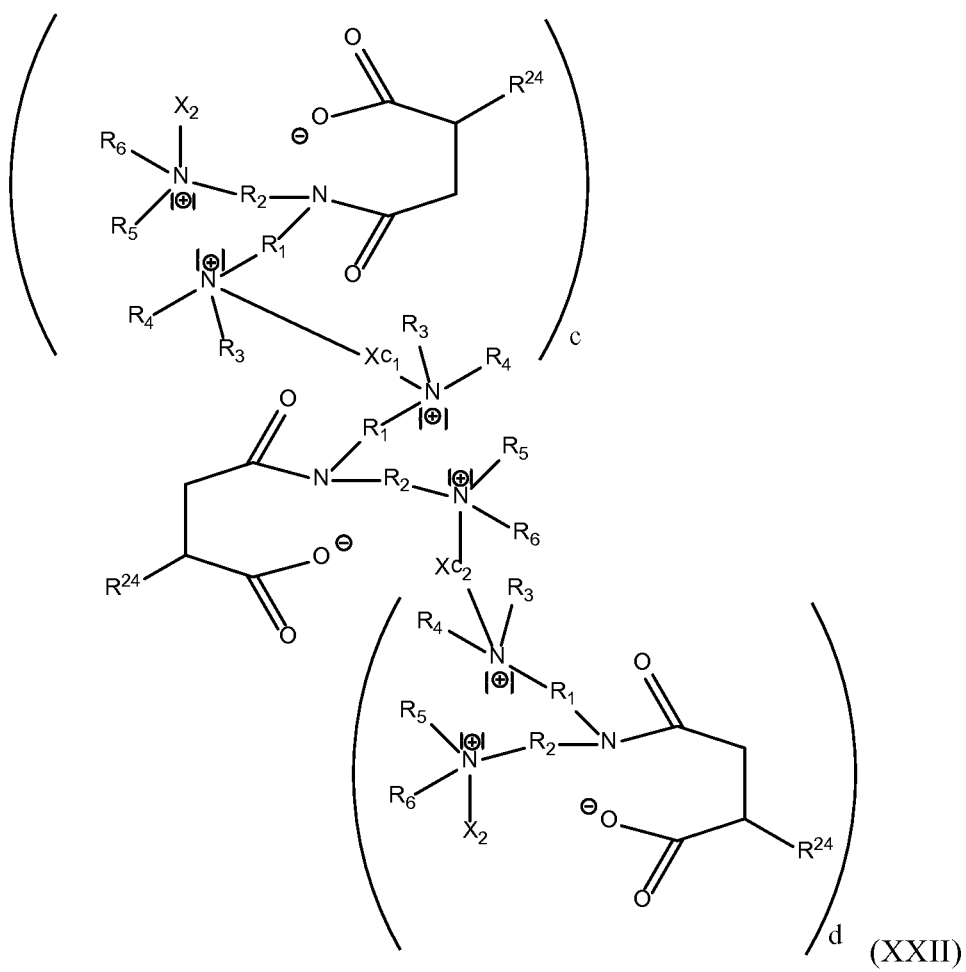


where a is an integer of from 2 to 8. An example of formula XXI where a is 2 or 3 can be represented, for example by formula XXI' and XXI'', respectively;



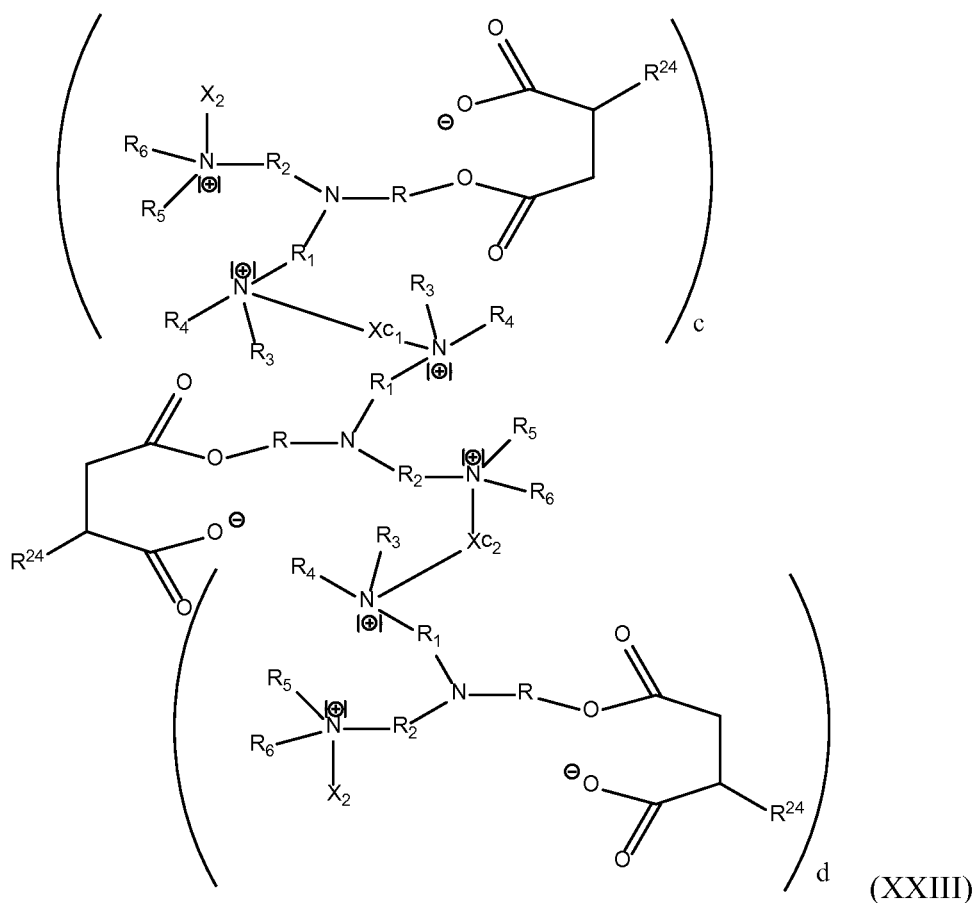
Further example coupled quaternary ammonium compounds can be, for example, as provided in formulas XXII and XXIII below:

-25-



where c and d are, individually, 0 or 1;

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where c and d are, individually, 0 or 1, and where R through R²⁴ and X1, X2, and Xc in each case are as defined above.

5 Compositions

[0093] In one embodiment, the present technology provides a composition comprising an amide or ester containing quaternary ammonium salt (high M_n amide/ester quat), and the use of the composition in a fuel composition to improve water shedding of the fuel composition. In another embodiment, the present technology provides a composition comprising an amide or ester containing quaternary ammonium salt, and the use of the composition in a lubricating composition with an oil of lubricating viscosity.

Fuel

[0094] The compositions of the present invention can comprise a fuel which is liquid at room temperature and is useful in fueling an engine. The fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30°C). The fuel can be a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel can be a

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petroleum distillate to include a gasoline as defined by EN228 or ASTM specification D4814, or a diesel fuel as defined by EN590 or ASTM specification D975. In an embodiment of the invention the fuel is a gasoline, and in other embodiments the fuel is a leaded gasoline, or a nonleaded gasoline. In another embodiment of this invention the fuel is a diesel fuel. The hydrocarbon fuel can be a hydrocarbon prepared by a gas to liquid process to include for example hydrocarbons prepared by a process such as the Fischer-Tropsch process. The nonhydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, to include an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof. The nonhydrocarbon fuel can include for example methanol, ethanol, methyl t-butyl ether, methyl ethyl ketone, transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane. Mixtures of hydrocarbon and nonhydrocarbon fuels can include for example gasoline and methanol and/or ethanol, diesel fuel and ethanol, and diesel fuel and a transesterified plant oil such as rapeseed methyl ester. In an embodiment of the invention the liquid fuel is an emulsion of water in a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. In several embodiments of this invention the fuel can have a sulfur content on a weight basis that is 5000 ppm or less, 1000 ppm or less, 300 ppm or less, 200 ppm or less, 30 ppm or less, or 10 ppm or less. In another embodiment the fuel can have a sulfur content on a weight basis of 1 to 100 ppm. In one embodiment the fuel contains 0 ppm to 1000 ppm, or 0 to 500 ppm, or 0 to 100 ppm, or 0 to 50 ppm, or 0 to 25 ppm, or 0 to 10 ppm, or 0 to 5 ppm of alkali metals, alkaline earth metals, transition metals or mixtures thereof. In another embodiment the fuel contains 1 to 10 ppm by weight of alkali metals, alkaline earth metals, transition metals or mixtures thereof. It is well known in the art that a fuel containing alkali metals, alkaline earth metals, transition metals or mixtures thereof have a greater tendency to form deposits and therefore foul or plug common rail injectors. The fuel of the invention is present in a fuel composition in a major amount that is generally greater than 50 percent by weight, and in other embodiments is present at greater than 90 percent by weight, greater than 95 percent by weight, greater than 99.5 percent by weight, or greater than 99.8 percent by weight.

[0095] Treat rates of the high M_n amide/ester quat to fuel range from 5 to 1000 ppm or 5 to 500 ppm, or 10 to 250 ppm, or 10 to 150 ppm, or 15 to 100 ppm. In other

embodiments the treat rate range may be from 250 to 1000 ppm, or 250 to 750 ppm, or 500 to 750 ppm, or 250 ppm to 500 ppm.

Oil of Lubricating Viscosity

[0096] In lubricating composition embodiments, the compositions of the present invention can comprise an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056]. A more detailed description of natural and synthetic lubricating oils is provided in paragraphs [0058] to [0059] respectively of WO2008/147704. Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to liquid synthetic procedure as well as other gas-to-liquid oils.

[0097] Oils of lubricating viscosity may also be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follow; Group I: > 0.03% sulfur or < 90% saturates and viscosity index 80-120; Group II: < 0.03% sulfur and $\geq$ 90% saturates and viscosity index 80-120; Group III: < 0.03% sulfur and $\geq$ 90% saturates and viscosity index $\geq$ 120; Group IV: all polyalphaolefins; Group V: all others. Groups I, II and III are typically referred to as mineral oil base stocks.

[0098] Typical treat rates of the high M_n amide/ester quat of the invention to lubricating oils is 0.1 to 10 wt% or 0.5 to 5wt % or 0.5 to 2.5wt % or 0.5 to 1 wt% or 0.1 to 0.5 wt% or 1 to 2 wt% based on a total weight of the lubricating oil.

[0099] 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 compound of the invention and the other performance additives.

[0100] The lubricating composition may be in the form of a concentrate and/or fully formulated lubricant. If the lubricating composition of the invention (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to from, in whole or in part, a finished lubricant), the ratio of the of these

additive to the oil of lubricating viscosity and/or diluent oil include the ranged of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

Miscellaneous

[0101] The fuel and/or lubricant compositions of the present invention include the high M_n amide/ester quats described above and may also include one or more additional additives. Such additional performance additives can be added to any of the compositions described depending on the results desired and the application in which the composition will be used.

[0102] Although any of the additional performance additives described herein can be used in any of the fuel and/or lubricant compositions of the invention, the following additional additives are particularly useful for fuel and/or lubricant compositions: antioxidants, corrosion inhibitors, detergent and/or dispersant additives other than those described above, cold flow improvers, foam inhibitors, demulsifiers, lubricity agents, metal deactivators, valve seat recession additives, biocides, antistatic agents, deicers, fluidizers, combustion improvers, seal swelling agents, wax control polymers, scale inhibitors, gas-hydrate inhibitors, or any combination thereof.

[0103] Demulsifiers suitable for use with the quaternary ammonium salts of the present technology can include, but not be limited to arylsulfonates and polyalkoxylated alcohol, such as, for example, polyethylene and polypropylene oxide copolymers and the like. The demulsifiers can also comprise nitrogen containing compounds such as oxazoline and imidazoline compounds and fatty amines, as well as Mannich compounds. Mannich compounds are the reaction products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: U.S. Pat. Nos. 3,036,003; 3,236,770; 3,414,347; 3,448,047; 3,461,172; 3,539,633; 3,586,629; 3,591,598; 3,634,515; 3,725,480; 3,726,882; and 3,980,569 herein incorporated by reference. Other suitable demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene oxide (EO) and

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propylene oxide (PO), for example including in the form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. In an embodiment there is no demulsifier present in the fuel and/or lubricant composition. The demulsifiers may be used alone or in combination. Some demulsifiers are commercially available, for example from Nalco or Baker Hughes.

[0104] Suitable antioxidants include for example hindered phenols or derivatives thereof and/or diarylamines or derivatives thereof. Suitable detergent/dispersant additives include for example polyetheramines or nitrogen containing detergents, including but not limited to PIB amine detergents/dispersants, succinimide detergents/dispersants, and other quaternary salt detergents/dispersants including polyisobutylsuccinimide-derived quaternized PIB/amine and/or amide dispersants/detergents. Suitable cold flow improvers include for example esterified copolymers of maleic anhydride and styrene and/or copolymers of ethylene and vinyl acetate. Suitable lubricity improvers or friction modifiers are based typically on fatty acids or fatty acid esters. Typical examples are tall oil fatty acid, as described, for example, in WO 98/004656, and glyceryl monooleate. The reaction products, described in U.S. Pat. No. 6,743,266 B2, of natural or synthetic oils, for example triglycerides, and alkanolamines are also suitable as such lubricity improvers. Additional examples include commercial tall oil fatty acids containing polycyclic hydrocarbons and/or rosin acids. Suitable metal deactivators include for example aromatic triazoles or derivatives thereof, including but not limited to benzotriazole. Other suitable metal deactivators are, for example, salicylic acid derivatives such as N,N'-disalicylidene-1,2-propanediamine. Suitable valve seat recession additives include for example alkali metal sulfosuccinate salts. Suitable foam inhibitors and/or antifoams include for example organic silicones such as polydimethyl siloxane, polyethylsiloxane, polydiethylsiloxane, polyacrylates and polymethacrylates, trimethyl-trifluoro-propylmethyl siloxane and the like. Suitable fluidizers include for example mineral oils and/or poly(alpha-olefins) and/or polyethers. Combustion improvers include for example octane and cetane improvers. Suitable cetane number improvers are, for example, aliphatic nitrates such as 2-ethylhexyl nitrate and cyclohexyl nitrate and peroxides such as di-tert-butyl peroxide.

[0105] The additional performance additives, which may be present in the fuel and/or lubricant compositions of the invention, also include di-ester, di-amide, ester-amide, and

ester-imide friction modifiers prepared by reacting an α -hydroxy acid with an amine and/or alcohol optionally in the presence of a known esterification catalyst. Examples of α -hydroxy acids include glycolic acid, lactic acid, α -hydroxy dicarboxylic acid (such as tartaric acid) and/or an α -hydroxy tricarboxylic acid (such as citric acid), with an amine and/or alcohol, optionally in the presence of a known esterification catalyst. These friction modifiers, often derived from tartaric acid, citric acid, or derivatives thereof, may be derived from amines and/or alcohols that are branched, resulting in friction modifiers that themselves have significant amounts of branched hydrocarbyl groups present within its structure. Examples of suitable branched alcohols used to prepare such friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, and mixtures thereof. Friction modifiers may be present at 0 to 6 wt % or 0.001 to 4 wt %, or 0.01 to 2 wt % or 0.05 to 3 wt % or 0.1 to 2 wt % or 0.1 to 1 wt % or 0.001 to 0.01 wt %.

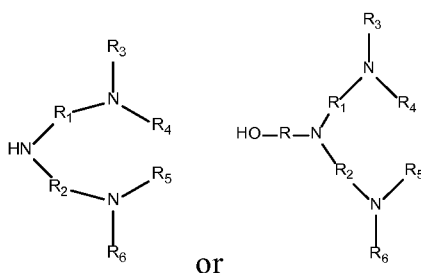
[0106] The additional performance additives may comprise a detergent/dispersant comprising a hydrocarbyl substituted acylating agent. The acylating agent may be, for example, a hydrocarbyl substituted succinic acid, or the condensation product of a hydrocarbyl substituted succinic acid with an amine or an alcohol; that is, a hydrocarbyl substituted succinimide or hydrocarbyl substituted succinate. In an embodiment, the detergent/dispersant may be a polyisobutenyl substituted succinic acid, amide or ester, wherein the polyisobutenyl substituent has a number average molecular weight of from about 100 to 5000. In some embodiments, the detergent may be a C₆ to C₁₈ substituted succinic acid, amide or ester. A more thorough description of the hydrocarbyl substituted acylating agent detergents can be found from paragraph [0017] to [0036] of U.S. Publication 2011/0219674, published September 15, 2011.

[0107] In one embodiment, the additional detergent/dispersant is a quaternary ammonium salts other than that of the present technology. The additional quaternary ammonium salts can be quaternary ammonium salts prepared from hydrocarbyl substituted acylating agents, such as, for example, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of from 300 to 750, or polyisobutyl succinic acids anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 1000 M_n.

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[0108] In an embodiment, the additional quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of from 300 to 750 is an amide or ester. In an embodiment, the quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n or, having a hydrocarbyl substituent with a number average molecular weight of from 300 to 750 is an imide.

[0109] In an embodiment the nitrogen containing compound of the additional quaternary ammonium salts is an imidazole or nitrogen containing compound of either of formulas.



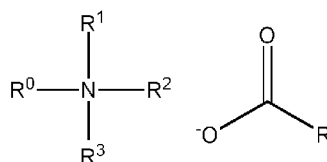
wherein R may be a C_1 to C_6 alkylene group; each of R_1 and R_2 , individually, may be a C_1 to C_6 hydrocarbylene group; and each of R_3 , R_4 , R_5 , and R_6 , individually, may be a hydrogen or a C_1 to C_6 hydrocarbyl group.

[0110] In other embodiments, the quaternizing agent used to prepare the additional quaternary ammonium salts can be a dialkyl sulfate, an alkyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, a carboxylate, alkyl esters, or mixtures thereof. In some cases the quaternizing agent can be a hydrocarbyl epoxide. In some cases the quaternizing agent can be a hydrocarbyl epoxide in combination with an acid. In some cases the quaternizing agent can be a salicylate, oxalate or terephthalate. In an embodiment the hydrocarbyl epoxide is an alcohol functionalized epoxides or C_4 to C_{14} epoxides.

[0111] In some embodiments, the quaternizing agent is multi-functional resulting in the additional quaternary ammonium salts being coupled quaternary ammoniums salts.

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[0112] Additional quaternary ammonium salts include, but are not limited to quaternary ammonium salts having a hydrophobic moiety in the anion. Exemplary compounds include quaternary ammonium compounds having the formula below:



wherein R^0 , R^1 , R^2 and R^3 is each individually an optionally substituted alkyl, alkenyl or aryl group and R includes an optionally substituted hydrocarbyl moiety having at least 5 carbon atoms.

[0113] Additional quaternary ammonium salts may also include polyetheramines that are the reaction products of a polyether-substituted amine comprising at least one tertiary quaternizable amino group and a quaternizing agent that converts the tertiary amino group to a quaternary ammonium group.

[0114] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercapthiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403.

[0115] The fuel and/or lubricant compositions of the invention may include a detergent additive, different from the disclosed high M_n amide/ester quat technology. Most conventional detergents used in the field of engine lubrication obtain most or all of their basicity or TBN from the presence of basic metal-containing compounds (metal hydroxides, oxides, or carbonates, typically based on such metals as calcium, magnesium, or sodium). Such metallic overbased detergents, also referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are typically prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid such as carbon dioxide) with a mixture of an acidic organic compound (also referred to as a substrate), a

stoichiometric excess of a metal base, typically in a reaction medium of an one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for the acidic organic substrate. Typically also a small amount of promoter such as a phenol or alcohol is present, and in some cases a small amount of water. The acidic organic substrate will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil.

[0116] Such conventional overbased materials and their methods of preparation are well known to those skilled in the art. Patents describing techniques for making basic metallic salts of sulfonic acids, carboxylic acids, phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. Salixarate detergents are described in U.S. patent 6,200,936. In certain embodiments, the detergent may contain a metal-containing salicylate detergent, such as an overbased calcium hydrocarbyl-substituted salicylate detergent and are described in U.S. Patents 5,688,751 and 4,627,928.

[0117] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the fuel and/or lubricant compositions of this invention. Viscosity improvers are usually polymers, including polyisobutenes, polymethacrylates (PMA) and polymethacrylic acid esters, hydrogenated diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins. PMA's are prepared from mixtures of methacrylate monomers having different alkyl groups. The alkyl groups may be either straight chain or branched chain groups containing from 1 to 18 carbon atoms. Most PMA's are viscosity modifiers as well as pour point depressants.

[0118] Multifunctional viscosity improvers, which also have dispersant and/or antioxidancy properties are known and may optionally be used in the fuel and/or lubricant compositions. Dispersant viscosity modifiers (DVM) are one example of such multifunctional additives. DVM are typically prepared by copolymerizing a small amount of a nitrogen-containing monomer with alkyl methacrylates, resulting in an additive with some combination of dispersancy, viscosity modification, pour point depressancy and dispersancy. Vinyl pyridine, N-vinyl pyrrolidone and N,N'-dimethylaminoethyl methacrylate are examples of nitrogen-containing monomers. Polyacrylates obtained from

the polymerization or copolymerization of one or more alkyl acrylates also are useful as viscosity modifiers.

[0119] Anti-wear agents may be used in the fuel and/or lubricant compositions provide herein. Anti-wear agents can in some embodiments include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2 or 0.015 to 0.15 or 0.02 to 0.1 or 0.025 to 0.08 percent by weight phosphorus. Often the antiwear agent is a zinc dialkyldithiophosphate (ZDP). For a typical ZDP, which may contain 11 percent P (calculated on an oil free basis), suitable amounts may include 0.09 to 0.82 percent by weight. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins. In some embodiments the fuel and/or lubricant compositions of the invention are free of phosphorus-containing antiwear/extreme pressure agents.

[0120] Foam inhibitors that may be useful in fuel and/or lubricant compositions of the invention include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. The disclosed technology may also be used with a silicone-containing antifoam agent in combination with a C₅ – C₁₇ alcohol.

[0121] Pour point depressants that may be useful in fuel and/or lubricant compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0122] Metal deactivators may be chosen from a derivative of benzotriazole (typically tolyltriazole), 1,2,4-triazole, benzimidazole, 2-alkyldithiobenzimidazole or 2-alkyldithiobenzothiazole, 1-amino-2-propanol, a derivative of dimercaptothiadiazole, octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and/or a fatty acid such as oleic acid with a polyamine.. The metal deactivators may also be described as corrosion inhibitors.

[0123] Seal swell agents include sulfolene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

Fuel Compositions

[0124] In some embodiments the technology provides fuel compositions. In some embodiments, the fuel compositions comprise a majority (>50 wt.%) of gasoline or a middle distillate fuel. In an embodiment, there is provided a fuel composition comprising a majority of a diesel fuel.

[0125] In yet another embodiment, the fuel composition comprises the high M_n amide/ester quats disclosed herein and a demulsifier. Demulsifiers suitable for use with the quaternary ammonium salts of the present technology can include, but not be limited to arylsulfonates and polyalkoxylated alcohol, such as, for example, polyethylene and polypropylene oxide copolymers and the like. The demulsifiers can also comprise nitrogen containing compounds such as oxazoline and imidazoline compounds and fatty amines, as well as Mannich compounds. Mannich compounds are the reaction products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: U.S. Pat. Nos. 3,036,003; 3,236,770; 3,414,347; 3,448,047; 3,461,172; 3,539,633; 3,586,629; 3,591,598; 3,634,515; 3,725,480; 3,726,882; and 3,980,569 herein incorporated by reference. Other suitable demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene oxide (EO) and propylene oxide (PO), for example including in the form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. In one embodiment the fuel composition of the invention does not comprise a demulsifier. The demulsifiers may be used alone or in combination. Some demulsifiers are commercially available, for example from Nalco or Baker Hughes. Typical treat rates of the demulsifiers to a fuel may range from 0 to 50 ppm by total weight of the fuel, or 5 to 50 ppm, or 5 to 25 ppm, or 5 to 20 ppm.

[0126] The disclosed technology may also be used with demulsifiers comprising a hydrocarbyl-substituted dicarboxylic acid in the form of the free acid, or in the form of the

anhydride which may be an intramolecular anhydride, such as succinic, glutaric, or phthalic anhydride, or an intermolecular anhydride linking two dicarboxylic acid molecules together. The hydrocarbyl substituent may have from 12 to 2000 carbon atoms and may include polyisobutenyl substituents having a number average molecular weight of 300 to 2800. Exemplary hydrocarbyl-substituted dicarboxylic acids include, but are not limited to, hydrocarbyl-substituted acids derived from malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, undecanedioic, dodecanedioic, phthalic, isophthalic, terphthalic, o-, m-, or p-phenylene diacetic, maleic, fumaric, or glutaconic acids.

[0127] In another embodiment, a fuel composition comprises the quaternary ammonium salts of the present invention and an additional detergent/dispersant. Customary detergent/dispersant additives are preferably amphiphilic substances which possess at least one hydrophobic hydrocarbon radical with a number-average molecular weight of 100 to 10000 and at least one polar moiety selected from (i) Mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties; (ii) Hydroxyl groups in combination with mono or polyamino groups, at least one nitrogen atoms having basic properties; (iii) Carboxyl groups or their alkali metal or alkaline earth metal salts; (iv) Sulfonic acid groups or their alkali metal or alkaline earth metal salts; (v) Polyoxy-C₂ to C₄ alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups; (vi) Carboxylic ester groups; (vii) Moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or (viii) Moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono-or polyamines.

[0128] The hydrophobic hydrocarbon radical in the above detergent/dispersant additives which ensures the adequate solubility in the fuel, has a number-average molecular weight (M_n) of 85 to 20,000, of 100 to 10,000, or 300 to 5000. In yet another embodiment, the detergent/dispersant additives have a M_n of 300 to 3000, of 500 to 2500, of 700 to 2500, or 800 to 1500. Typical hydrophobic hydrocarbon radicals may be polypropenyl, polybutenyl and polyisobutenyl radicals, with a number average molecular weight M_n , of 300 to 5000, of 300 to 3000, of 500 to 2500, or 700 to 2500. In one embodiment the detergent/dispersant additives have a M_n of 800 to 1500.

[0129] The additional performance additives may comprise a high TBN nitrogen containing detergent/dispersant, such as a succinimide, that is the condensation product of

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a hydrocarbyl-substituted succinic anhydride with a poly(alkyleneamine). Succinimide detergents/dispersants are more fully described in U.S. patents 4,234,435 and 3,172,892. Another class of ashless dispersant is high molecular weight esters, prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0130] Nitrogen-containing detergents are the reaction products of a carboxylic acid-derived acylating agent and an amine. The acylating agent can vary from formic acid and its acylating derivatives to acylating agents having high molecular weight aliphatic substituents of up to 5,000, 10,000 or 20,000 carbon atoms. The amino compounds can vary from ammonia itself to amines typically having aliphatic substituents of up to about 30 carbon atoms, and up to 11 nitrogen atoms. Acylated amino compounds suitable for use in the present invention can be those formed by the reaction of an acylating agent having a hydrocarbyl substituent of at least 8 carbon atoms and a compound comprising at least one primary or secondary amine group. The acylating agent may be a mono- or polycarboxylic acid (or reactive equivalent thereof) for example a substituted succinic, phthalic or propionic acid and the amino compound may be a polyamine or a mixture of polyamines, for example a mixture of ethylene polyamines. Alternatively the amine may be a hydroxyalkyl-substituted polyamine. The hydrocarbyl substituent in such acylating agents may comprise at least 10 carbon atoms. In one embodiment, the hydrocarbyl substituent may comprise at least 12, for example 30 or 50 carbon atoms. In yet another embodiment, it may comprise up to 200 carbon atoms. The hydrocarbyl substituent of the acylating agent may have a number average molecular weight (M_n) of 170 to 2800, for example from 250 to 1500. In other embodiments, the substituent's M_n may range from 500 to 1500, or alternatively from 500 to 1100. In yet another embodiment, the substituent's M_n may range from 700 to 1300. In another embodiment, the hydrocarbyl substituent may have a number average molecular weight of 700 to 1000, or 700 to 850, or, for example, 750.

[0131] Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde and are described in more detail in U.S. Patent 3,634,515.

[0132] A useful nitrogen containing dispersant includes the product of a Mannich reaction between (a) an aldehyde, (b) a polyamine, and (c) an optionally substituted phenol. The phenol may be substituted such that the Mannich product has a molecular weight of less than 7500. Optionally, the molecular weight may be less than 2000, less than 1500, less than 1300, or for example, less than 1200, less than 1100, less than 1000. In some embodiments, the Mannich product has a molecular weight of less than 900, less than 850, or less than 800, less than 500, or less than 400. The substituted phenol may be substituted with up to 4 groups on the aromatic ring. For example it may be a tri or di-substituted phenol. In some embodiments, the phenol may be a mono-substituted phenol. The substitution may be at the ortho, and/or meta, and/or para position(s). To form the Mannich product, the molar ratio of the aldehyde to amine is from 4:1 to 1:1 or, from 2:1 to 1:1. The molar ratio of the aldehyde to phenol may be at least 0.75:1; or 0.75 to 1 to 4:1, or 1:1 to 4:1, or 1:1 to 2:1. To form the preferred Mannich product, the molar ratio of the phenol to amine can be at least 1.5:1, at least 1.6:1, at least 1.7:1, for example at least 1.8:1, or at least 1.9:1. The molar ratio of phenol to amine may be up to 5:1; for example it may be up to 4:1, or up to 3.5:1. Suitably it is up to 3.25:1, up to 3:1, up to 2.5:1, up to 2.3:1 or up to 2.1:1.

[0133] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer. An amine is typically employed in preparing the high TBN nitrogen-containing dispersant. One or more poly(alkyleneamine)s may be used, and these may comprise one or more poly(ethyleneamine)s having 3 to 5 ethylene units and 4 to 6 nitrogen units. Such materials include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA). Such materials are typically commercially available as mixtures of various isomers containing a range number of ethylene units and nitrogen atoms, as well as a variety of isomeric structures, including various cyclic structures. The poly(alkyleneamine) may likewise comprise relatively higher molecular weight amines known in the industry as ethylene amine still bottoms.

[0134] In an embodiment, the fuel composition can additionally comprise quaternary ammonium salts other than those of the present technology. The other quaternary ammonium salts can comprise (a) a compound comprising (i) at least one tertiary amino

group as described above, and (ii) a hydrocarbyl-substituent having a number average molecular weight of 100 to 5000, or 250 to 4000, or 100 to 4000 or 100 to 2500 or 3000; and (b) a quaternizing agent suitable for converting the tertiary amino group of (a)(i) to a quaternary nitrogen, as described above. The other quaternary ammonium salts are more thoroughly described in U.S. Patent Nos. 7,951,211, issued May 31, 2011, and 8,083,814, issued December 27, 2011, and U.S. Publication Nos. 2013/0118062, published May 16, 2013, 2012/0010112, published January 12, 2012, 2013/0133243, published May 30, 2013, 2008/0113890, published May 15, 2008, and 2011/0219674, published September 15, 2011, US 2012/0149617 published May 14, 2012, US 2013/0225463 published August 29, 2013, US 2011/0258917 published October 27, 2011, US 2011/0315107 published December 29, 2011, US 2013/0074794 published March 28, 2013, US 2012/0255512 published October 11, 2012, US 2013/0333649 published December 19, 2013, US 2013/0118062 published May 16, 2013, and international publications WO Publication Nos. 2011/141731, published November 17, 2011, 2011/095819, published August 11, 2011, and 2013/017886, published February 7, 2013, WO 2013/070503 published May 16, 2013, WO 2011/110860 published September 15, 2011, WO 2013/017889 published February 7, 2013, WO 2013/017884 published February 7, 2013.

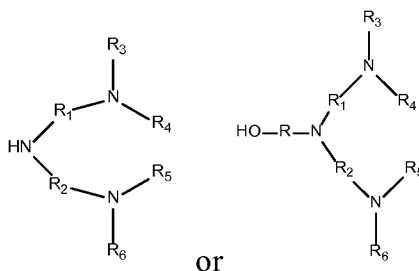
[0135] The additional quaternary ammonium salts other than the disclosed technology can be quaternary ammonium salts prepared from hydrocarbyl substituted acylating agents, such as, for example, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n , polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750, or polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 1000 M_n .

[0136] In an embodiment, the fuel composition comprising the quaternary ammonium salts of this invention can further comprise an additional quaternary ammonium salts prepared from the reaction of a nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of 300 to 750 is an amide or ester. In an embodiment, the quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a

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hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n or, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750 is an imide.

[0137] In an embodiment the nitrogen containing compound of the additional quaternary ammonium salts is an imidazole or nitrogen containing compound of either of formulas.



wherein R may be a C_1 to C_6 alkylene group; each of R_1 and R_2 , individually, may be a C_1 to C_6 hydrocarbylene group; and each of R_3 , R_4 , R_5 , and R_6 , individually, may be a hydrogen or a C_1 to C_6 hydrocarbyl group.

[0138] In other embodiments, the quaternizing agent used to prepare the additional quaternary ammonium salts can be a dialkyl sulfate, an alkyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, a carboxylate, alkyl esters, or mixtures thereof. In some cases the quaternizing agent can be a hydrocarbyl epoxide. In some cases the quaternizing agent can be a hydrocarbyl epoxide in combination with an acid. In some cases the quaternizing agent can be a salicylate, oxalate or terephthalate. In an embodiment the hydrocarbyl epoxide is an alcohol functionalized epoxides or C_4 to C_{14} epoxides, or C_4 or C_{20} epoxides.

[0139] In some embodiments, the quaternizing agent is multi-functional resulting in the additional quaternary ammonium salts being a coupled quaternary ammoniums salts.

[0140] Typical treat rates of additional detergents/dispersants to a fuel of the invention is 0 to 500 ppm, or 0 to 250 ppm, or 0 to 100 ppm, or 5 to 250 ppm, or 5 to 100 ppm, or 10 to 100 ppm.

[0141] In a particular embodiment, a fuel composition comprises the quaternary ammonium salts of the present invention and a cold flow improver. The cold flow improver is typically selected from (1) copolymers of a C_2 - to C_{40} -olefin with at least one

further ethylenically unsaturated monomer; (2) comb polymers; (3) polyoxyalkylenes; (4) polar nitrogen compounds; (5) sulfocarboxylic acids or sulfonic acids or derivatives thereof; and (6) poly(meth)acrylic esters.

[0142] It is possible to use either mixtures of different representatives from one of the particular classes (1) to (6) or mixtures of representatives from different classes (1) to (6).

[0143] Suitable C₂- to C₄₀-olefin monomers for the copolymers of class (1) are, for example, those having 2 to 20 and especially 2 to 10 carbon atoms, and 1 to 3 and preferably 1 or 2 carbon-carbon double bonds, especially having one carbon-carbon double bond. In the latter case, the carbon-carbon double bond may be arranged either terminally (α -olefins) or internally. However, preference is given to α -olefins, more preferably α -olefins having 2 to 6 carbon atoms, for example propene, 1-butene, 1-pentene, 1-hexene and in particular ethylene. The at least one further ethylenically unsaturated monomer of class (1) is preferably selected from alkenyl carboxylates; for example, C₂- to C₁₄-alkenyl esters, for example the vinyl and propenyl esters, of carboxylic acids having 2 to 21 carbon atoms, whose hydrocarbon radical may be linear or branched among these, preference is given to the vinyl esters, examples of suitable alkenyl carboxylates are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl neopentanoate, vinyl hexanoate, vinyl neononanoate, vinyl neodecanoate and the corresponding propenyl esters, (meth)acrylic esters; for example, esters of (meth)acrylic acid with C₁- to C₂₀-alkanols, especially C₁- to C₁₀-alkanols, in particular with methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol and decanol, and structural isomers thereof and further olefins; preferably higher in molecular weight than the abovementioned C₂- to C₄₀-olefin base monomer for example, the olefin base monomer used is ethylene or propene, suitable further olefins are in particular C₁₀- to C₄₀- α -olefins.

[0144] Suitable copolymers of class (1) are also those which comprise two or more different alkenyl carboxylates in copolymerized form, which differ in the alkenyl function and/or in the carboxylic acid group. Likewise suitable are copolymers which, as well as the alkenyl carboxylate(s), comprise at least one olefin and/or at least one (meth)acrylic ester in copolymerized form.

[0145] Terpolymers of a C₂- to C₄₀- α -olefin, a C₁- to C₂₀-alkyl ester of an ethylenically unsaturated monocarboxylic acid having 3 to 15 carbon atoms and a C₂- to C₁₄-alkenyl

ester of a saturated monocarboxylic acid having 2 to 21 carbon atoms are also suitable as copolymers of class (K1). Terpolymers of this kind are described in WO 2005/054314. A typical terpolymer of this kind is formed from ethylene, 2-ethylhexyl acrylate and vinyl acetate.

5 [0146] The at least one or the further ethylenically unsaturated monomer(s) are copolymerized in the copolymers of class (1) in an amount of preferably 1 to 50% by weight, especially 10 to 45% by weight and in particular 20 to 40% by weight, based on the overall copolymer. The main proportion in terms of weight of the monomer units in the copolymers of class (1) therefore originates generally from the C₂ to C₄₀ base olefins.
10 The copolymers of class (1) can have a number-average molecular weight M_n of 1000 to 20,000, or 1000 to 10,000, or 1000 to 8000.

[0147] Typical comb polymers of component (2) are, for example, obtainable by the copolymerization of maleic anhydride or fumaric acid with another ethylenically unsaturated monomer, for example with an α -olefin or an unsaturated ester, such as vinyl acetate, and subsequent esterification of the anhydride or acid function with an alcohol
15 having at least 10 carbon atoms. Further suitable comb polymers are copolymers of α -olefins and esterified comonomers, for example esterified copolymers of styrene and maleic anhydride or esterified copolymers of styrene and fumaric acid. Suitable comb polymers may also be polyfumarates or polymaleates. Homo- and copolymers of vinyl
20 ethers are also suitable comb polymers. Comb polymers suitable as components of class (2) are, for example, also those described in WO 2004/035715 and in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs. 8, pages 117 to 253 (1974). Mixtures of comb polymers are also suitable.

25 [0148] Polyoxyalkylenes suitable as components of class (3) are, for example, polyoxyalkylene esters, polyoxyalkylene ethers, mixed polyoxyalkylene ester/ethers and mixtures thereof. These polyoxyalkylene compounds preferably comprise at least one linear alkyl group, preferably at least two linear alkyl groups, each having 10 to 30 carbon atoms and a polyoxyalkylene group having a number-average molecular weight of up to
30 5000. Such polyoxyalkylene compounds are described, for example, in EP-A 061 895 and also in U.S. Pat. No. 4,491,455. Particular polyoxyalkylene compounds are based on polyethylene glycols and polypropylene glycols having a number-average molecular

weight of 100 to 5000. Additionally suitable are polyoxyalkylene mono- and diesters of fatty acids having 10 to 30 carbon atoms, such as stearic acid or behenic acid.

[0149] Polar nitrogen compounds suitable as components of class (4) may be either ionic or nonionic and may have at least one substituent, in particular at least two substituents, in the form of a tertiary nitrogen atom of the general formula $>NR^7$ in which R^7 is a C_8 - to C_{40} -hydrocarbon radical. The nitrogen substituents may also be quaternized i.e. be in cationic form. An example of such nitrogen compounds is that of ammonium salts and/or amides which are obtainable by the reaction of at least one amine substituted by at least one hydrocarbon radical with a carboxylic acid having 1 to 4 carboxyl groups or with a suitable derivative thereof. The amines may comprise at least one linear C_8 - to C_{40} -alkyl radical. Primary amines suitable for preparing the polar nitrogen compounds mentioned are, for example, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tetradecylamine and the higher linear homologs. Secondary amines suitable for this purpose are, for example, dioctadecylamine and methylbehenylamine. Also suitable for this purpose are amine mixtures, in particular amine mixtures obtainable on the industrial scale, such as fatty amines or hydrogenated tallamines, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, "Amines, aliphatic" chapter. Acids suitable for the reaction are, for example, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalene dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and succinic acids substituted by long-chain hydrocarbon radicals.

[0150] Sulfocarboxylic acids, sulfonic acids or derivatives thereof which are suitable as cold flow improvers of class (5) are, for example, the oil-soluble carboxamides and carboxylic esters of ortho-sulfobenzoic acid, in which the sulfonic acid function is present as a sulfonate with alkyl-substituted ammonium cations, as described in EP-A 261 957.

[0151] Poly(meth)acrylic esters suitable as cold flow improvers of class (6) are either homo- or copolymers of acrylic and methacrylic esters. Preference is given to copolymers of at least two different (meth)acrylic esters which differ with regard to the esterified alcohol. The copolymer optionally comprises another different olefinically unsaturated monomer in copolymerized form. The weight-average molecular weight of the polymer can be 50,000 to 500,000. The polymer can be a copolymer of methacrylic acid and methacrylic esters of saturated C_{14} and C_{15} alcohols, the acid groups having been

neutralized with hydrogenated tallamine. Suitable poly(meth)acrylic esters are described, for example, in WO 00/44857.

[0152] The cold flow improver or the mixture of different cold flow improvers is added to the middle distillate fuel or diesel fuel in a total amount of preferably 0 to 5000ppm by weight, or 10 to 5000 ppm by weight, or 20 to 2000 ppm by weight, or 50 to 1000 ppm by weight or 100 to 700 ppm by weight, for example of 200 to 500 ppm by weight.

Engine Oil Lubricants

[0153] In different embodiments the technology provides engine oil lubricating compositions that can be employed in internal combustion engines. The internal combustion engine may be spark ignition or compression ignition. The internal combustion engine may be a 2-stroke or 4-stroke engine. The internal combustion engine may be a passenger car engine, a light duty diesel engine, a heavy duty diesel engine, a motorcycle engine, or a 2-stroke or 4-stroke marine diesel engine. Typically the internal combustion engine may be a passenger car engine, or a heavy duty diesel internal combustion engine.

[0154] In one embodiment an engine oil lubricant composition of the invention comprises in addition to the quaternary ammonium salts of the present technology an overbased metal-containing detergent, or mixtures thereof.

[0155] Overbased detergents are known in the art. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, typically carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a calcium chloride, acetic acid, phenol or alcohol. The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of "excess" metal (stoichiometrically) is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to

the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5. The term "metal ratio is also explained in standard textbook entitled "Chemistry and Technology of Lubricants", Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, page 219, sub-heading 7.25.

[0156] The overbased metal-containing detergent may be chosen from non-sulfur-containing phenates, sulfur-containing phenates, sulfonates, salixarates, salicylates, carboxylates, and mixtures thereof, or borated equivalents thereof. The overbased detergent may be borated with a borating agent such as boric acid. The overbased detergent may be non-sulfur containing phenates, sulfur containing phenates, sulfonates, or mixtures thereof.

[0157] An engine oil lubricant may further comprise an overbased sulfonate detergent present at 0.01 wt % to 0.9 wt %, or 0.05 wt % to 0.8 wt %, or 0.1 wt % to 0.7 wt %, or 0.2 wt % to 0.6 wt %.

[0158] The overbased sulfonate detergent may have a metal ratio of 12 to less than 20, or 12 to 18, or 20 to 30, or 22 to 25.

[0159] An engine oil lubricant composition may also include one or more detergents in addition to the overbased sulfonate.

[0160] Overbased sulfonates typically have a total base number of 250 to 600, or 300 to 500 (on an oil free basis). Overbased detergents are known in the art. In one embodiment the sulfonate detergent may be a predominantly linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Application 2005065045 (and granted as US 7,407,919). Linear alkyl benzenes may have the benzene ring attached anywhere on the linear chain, usually at the 2, 3, or 4 position, or mixtures thereof. The predominantly linear alkylbenzene sulfonate detergent may be particularly useful for assisting in improving fuel economy. In one embodiment the sulfonate detergent may be a metal salt of one or more oil-soluble alkyl toluene sulfonate compounds as disclosed in paragraphs [0046] to [0053] of US Patent Application 2008/0119378.

[0161] In one embodiment the overbased sulfonate detergent comprises an overbased calcium sulfonate. The calcium sulfonate detergent may have a metal ratio of 18 to 40 and a TBN of 300 to 500, or 325 to 425.

[0162] The other detergents may have a metal of the metal-containing detergent may also include "hybrid" detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described; for example, in US
5 Patents 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a hybrid sulfonate/phenate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0163] The other detergent may have an alkali metal, an alkaline earth metal, or zinc
10 counter ion. In one embodiment the metal may be sodium, calcium, barium, or magnesium. Typically other detergent may be sodium, calcium, or magnesium containing detergent (typically, calcium, or magnesium containing detergent).

[0164] The other detergent may typically be an overbased detergent of sodium,
15 calcium or magnesium salt of the phenates, sulfur-containing phenates, salixarates and salicylates. Overbased phenates and salicylates typically have a total base number of 180 to 450 TBN (on an oil free basis).

[0165] Phenate detergents are typically derived from p-hydrocarbyl phenols. Alkylphenols of this type may be coupled with sulfur and overbased, coupled with aldehyde and overbased, or carboxylated to form salicylate detergents. Suitable
20 alkylphenols include those alkylated with oligomers of propylene, i.e. tetrapropenylphenol (i.e. p-dodecylphenol or PDDP) and pentapropenylphenol. Other suitable alkylphenols include those alkylated with alpha-olefins, isomerized alpha-olefins, and polyolefins like polyisobutylene. In one embodiment, the lubricating composition comprises less than 0.2 wt %, or less than 0.1 wt %, or even less than 0.05 wt % of a phenate detergent derived
25 from PDDP. In one embodiment, the lubricant composition comprises a phenate detergent that is not derived from PDDP.

[0166] The overbased detergent may be present at 0 wt % to 10 wt %, or 0.1 wt % to
30 10 wt %, or 0.2 wt % to 8 wt %, or 0.2 wt % to 3 wt %. For example in a heavy duty diesel engine the detergent may be present at 2 wt % to 3 wt % of the lubricant composition. For a passenger car engine the detergent may be present at 0.2 wt % to 1 wt % of the lubricant composition. In one embodiment, an engine oil lubricant composition comprises at least one overbased detergent with a metal ratio of at least 3, or at least 8, or at least 15.

[0167] In an embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology may further include a dispersant, or mixtures thereof. The dispersant may be chosen from a succinimide dispersant, a Mannich dispersant, a succinamide dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof.

[0168] In one embodiment an engine oil lubricant composition includes a dispersant or mixtures thereof. The dispersant may be present as a single dispersant. The dispersant may be present as a mixture of two or more (typically two or three) different dispersants, wherein at least one may be a succinimide dispersant.

[0169] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be chosen from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0170] In one embodiment the dispersant may be a polyolefin succinic acid ester, amide, or ester-amide. For instance, a polyolefin succinic acid ester may be a polyisobutylene succinic acid ester of pentaerythritol, or mixtures thereof. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and an amine (such as a diamine, typically diethyleneamine).

[0171] The dispersant may be an N-substituted long chain alkenyl succinimide. An example of an N-substituted long chain alkenyl succinimide is polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic anhydride may be derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. Succinimide dispersants and their preparation are disclosed, for instance in US Patents 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, 7,238,650 and EP Patent Application 0 355 895 A.

[0172] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid),

urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, and ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment the post-treated dispersant is borated. In one embodiment the post-treated dispersant may be reacted with dimercaptothiadiazoles. In one embodiment the post-treated dispersant may be reacted with phosphoric or phosphorous acid. In one embodiment the post-treated dispersant may be reacted with terephthalic acid and boric acid (as described in US Patent Application US2009/0054278).

[0173] In one embodiment the dispersant may be borated or non-borated. Typically a borated dispersant may be a succinimide dispersant. In one embodiment, the ashless dispersant may be boron-containing, i.e., has incorporated boron and delivers said boron to the lubricant composition. The boron-containing dispersant may be present in an amount to deliver at least 25 ppm boron, at least 50 ppm boron, or at least 100 ppm boron to the lubricant composition. In one embodiment, the lubricant composition may be free of a boron-containing dispersant, i.e. delivers no more than 10 ppm boron to the final formulation.

[0174] The dispersant may be prepared/obtained/obtainable from reaction of succinic anhydride by an "ene" or "thermal" reaction, by what may be referred to as a "direct alkylation process." The "ene" reaction mechanism and general reaction conditions are summarized in "Maleic Anhydride", pages, 147-149, Edited by B.C. Trivedi and B.C. Culbertson and Published by Plenum Press in 1982. The dispersant prepared by a process that includes an "ene" reaction may be a polyisobutylene succinimide having a carbocyclic ring present on less than 50 mole %, or 0 to less than 30 mole %, or 0 to less than 20 mole %, or 0 mole % of the dispersant molecules. The "ene" reaction may have a reaction temperature of 180 °C to less than 300 °C, or 200 °C to 250 °C, or 200 °C to 220 °C.

[0175] The dispersant may also be obtained/obtainable from a chlorine-assisted process, often involving Diels-Alder chemistry, leading to formation of carbocyclic linkages. The process is known to a person skilled in the art. The chlorine-assisted process may produce a dispersant that is a polyisobutylene succinimide having a carbocyclic ring present on 50 mole % or more, or 60 to 100 mole % of the dispersant molecules. Both the thermal and chlorine-assisted processes are described in greater detail in U.S. Patent 7,615,521, columns 4-5 and preparative examples A and B.

[0176] The dispersant may have a carbonyl to nitrogen ratio (CO:N ratio) of 5:1 to 1:10, 2:1 to 1:10, or 2:1 to 1:5, or 2:1 to 1:2. In one embodiment the dispersant may have a CO:N ratio of 2:1 to 1:10, or 2:1 to 1:5, or 2:1 to 1:2, or 1:1.4 to 1:0.6.

[0177] In one embodiment the dispersant may be a succinimide dispersant may comprise a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 350 to 5000, or 750 to 2500.

[0178] The dispersant may be present at 0 wt % to 20 wt %, 0.1 wt % to 15 wt %, or 0.5 wt % to 9 wt %, or 1 wt % to 8.5 wt % or 1.5 to 5 wt % of the lubricant composition.

[0179] In one embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology may be a lubricant composition further comprising a molybdenum compound. The molybdenum compound may be an antiwear agent or an antioxidant. The molybdenum compound may be chosen from molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof. The molybdenum compound may provide the lubricant 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.

[0180] In another embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology may further comprise an antioxidant.

Antioxidants include sulfurized olefins, diarylamines, alkylated diarylamines, hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), hydroxyl thioethers, or mixtures thereof. In one embodiment the lubricant composition includes an antioxidant, or mixtures thereof. The antioxidant may be present at 0 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 0.5 wt % to 5 wt %, or 0.5 wt % to 3 wt %, or 0.3 wt % to 1.5 wt % of the lubricant composition.

[0181] In one embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology further comprises a phenolic or an aminic antioxidant or mixtures thereof, and wherein the antioxidant is present at 0.1 wt % to 3 wt %, or 0.5 wt % to 2.75 wt %, or 1 wt % to 2.5 wt %.

[0182] The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnaphthylamine, or mixtures

thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In one embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include octyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenyl-naphthylamines.

[0183] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0184] Examples of molybdenum dithiocarbamates, which may be used as an antioxidant, include commercial materials sold under the trade names such as Molyvan 822®, Molyvan® A and Molyvan® 855 from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165, S-600 and 525, or mixtures thereof.

[0185] In one embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology further includes a viscosity modifier. The viscosity modifier is known in the art and may include hydrogenated styrene-butadiene rubbers, ethylene-propylene copolymers, ethylene copolymers with propylene and higher olefins, polymethacrylates, polyacrylates, hydrogenated styrene-isoprene polymers, hydrogenated diene polymers, polyalkyl styrenes, polyolefins, esters of maleic anhydride-olefin copolymers (such as those described in International Application WO 2010/014655), esters of maleic anhydride-styrene copolymers, or mixtures thereof. The viscosity modifier may include a block copolymer comprising (i) a vinyl aromatic monomer block and (ii), a conjugated diene olefin monomer block (such as a hydrogenated

styrene-butadiene copolymer or a hydrogenated styrene-isoprene copolymer), a polymethacrylate, an ethylene- α olefin copolymer, a hydrogenated star polymer comprising conjugated diene monomers such as butadiene or isoprene, or a star polymer of polymethacrylate, or mixtures thereof.

5 [0186] In an embodiment the viscosity modifier may be a dispersant viscosity modifier. The dispersant viscosity modifier may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine.

10 [0187] In one embodiment the dispersant viscosity modifier comprises an olefin copolymer further functionalized with a dispersant amine group. Typically, the olefin copolymer is an ethylene-propylene copolymer. The olefin copolymer has a number average molecular weight of 5000 to 20,000, or 6000 to 18,000, or 7000 to 15,000.

[0188] The olefin copolymer may have a shear stability index of 0 to 20, or 0 to 10, or 0 to 5 as measured by the Orbahn shear test (ASTM D6278) as described above.

15 [0189] The formation of a dispersant viscosity modifier is well known in the art. The dispersant viscosity modifier may include for instance those described in U.S. Patent US 7,790,661 column 2, line 48 to column 10, line 38. In one embodiment the dispersant viscosity modifier may be prepared by grafting of an olefinic carboxylic acid acylating agent onto a polymer of 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of
20 C₃₋₁₀ α -monoolefin, and from 0 to 15 mole percent of non-conjugated diene or triene, said polymer having an average molecular weight ranging from 5000 to 20,000, and further reacting said grafted polymer with an amine (typically an aromatic amine).

25 [0190] The dispersant viscosity modifier may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalized with an amine, or styrene-maleic anhydride copolymers reacted with an amine. Suitable amines may be aliphatic or aromatic amines and polyamines. Examples of suitable aromatic amines include nitroaniline, aminodiphenylamine (ADPA), hydrocarbylene coupled polyaromatic amines, and mixtures thereof. More detailed description of dispersant
30 viscosity modifiers are disclosed in International Publication WO2006/015130 or U.S. Patents 4,863,623; 6,107,257; 6,107,258; 6,117,825; and US 7,790,661.

[0191] In one embodiment the dispersant viscosity modifier may include those described in U.S. Patent 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described paragraphs [0065] to [0073]). In one embodiment the dispersant viscosity modifier may include those described in U.S. Patent US 7,790,661 column 2, line 48 to column 10, line 38.

[0192] In one embodiment an engine oil lubricant composition of the invention further comprises a dispersant viscosity modifier. The dispersant viscosity modifier may be present at 0 wt % to 5 wt %, or 0 wt % to 4 wt %, or 0.05 wt % to 2 wt %, or 0.2 wt % to 1.2 wt % of the lubricant composition.

[0193] In one embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology further includes a friction modifier.

[0194] In one embodiment the friction modifier may be chosen from long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; fatty alkyl tartramides; fatty malic esters and imides, fatty (poly)glycolates; and fatty glycolamides. The friction modifier may be present at 0 wt % to 6 wt %, or 0.01 wt % to 4 wt %, or 0.05 wt % to 2 wt %, or 0.1 wt % to 2 wt % of the lubricant composition. As used herein the term "fatty alkyl" or "fatty" in relation to friction modifiers means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain.

[0195] Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; fatty alkyl tartramides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters such as glycerol mono-oleate; borated glycerol esters; fatty amines; alkoxylated fatty amines; borated alkoxylated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxylated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0196] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

5 [0197] 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 mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0198] An engine oil lubricant composition comprising the quaternary ammonium salts of the present technology optionally further includes at least one antiwear agent.

10 [0199] Examples of suitable antiwear agents include titanium compounds, tartaric acid derivatives such as tartrate esters, amides or tartrides, malic acid derivatives, citric acid derivatives, glycolic acid derivatives, oil soluble amine salts of phosphorus compounds different from that of the invention, sulfurized olefins, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), phosphites (such as dibutyl phosphite),
15 phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides.

[0200] The antiwear agent may in one embodiment include a tartrate or tartride as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125.
20 The tartrate or tartride may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in US Patent Application 20050198894.

[0201] Another class of additives includes oil-soluble titanium compounds as disclosed in US 7,727,943 and US2006/0014651. The oil-soluble titanium compounds
25 may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In one embodiment the oil soluble titanium compound is a titanium (IV) alkoxide. The titanium alkoxide is formed from a monohydric alcohol, a polyol or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms. In one embodiment, the titanium alkoxide is titanium (IV) isopropoxide.
30 In one embodiment, the titanium alkoxide is titanium (IV) 2-ethylhexoxide. In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. In one embodiment, the 1,2-vicinal diol comprises a fatty acid mono-ester of glycerol,

often the fatty acid is oleic acid. In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In one embodiment the titanium (IV) carboxylate is titanium neodecanoate.

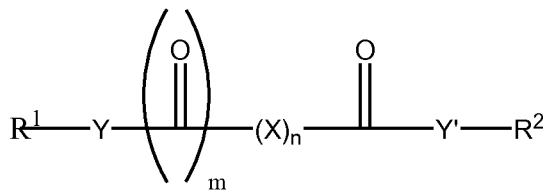
[0202] An engine oil lubricant composition comprising the quaternary ammonium salts of the present technology may further include a phosphorus-containing antiwear agent different from that of the invention. Typically the phosphorus-containing antiwear agent may be a zinc dialkyldithiophosphate, phosphite, phosphate, phosphonate, and ammonium phosphate salts, or mixtures thereof.

[0203] In one embodiment an engine oil lubricant composition may further comprise a phosphorus-containing antiwear agent, typically zinc dialkyldithiophosphate. Zinc dialkyldithiophosphates are known in the art. Examples of zinc dithiophosphates include zinc isopropyl methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, zinc di(cyclohexyl) dithiophosphate, zinc isobutyl 2-ethylhexyl dithiophosphate, zinc isopropyl 2-ethylhexyl dithiophosphate, zinc isobutyl isoamyl dithiophosphate, zinc isopropyl n-butyl dithiophosphate, and combinations thereof. Zinc dialkyldithiophosphate may be present in amount to provide 0.01 wt % to 0.1 wt % phosphorus to the lubricating composition, or to provide 0.015 wt % to 0.075 wt % phosphorus, or 0.02 wt % to 0.05 wt % phosphorus to the lubricating composition.

[0204] In one embodiment, an engine oil lubricant composition further comprises one or more zinc dialkyldithiophosphate such that the amine (thio)phosphate additive of the invention provides at least 50% of the total phosphorus present in the lubricating composition, or at least 70% of the total phosphorus, or at least 90% of the total phosphorus in the lubricating composition. In one embodiment, the lubricant composition is free or substantially free of a zinc dialkyldithiophosphate. The antiwear agent may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 0.9 wt % of the lubricant composition.

[0205] In one embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology further comprises 0.01 to 5 wt % or 0.1 to 2 wt % of an ashless antiwear agent represented by Formula:

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wherein

Y and Y' are independently -O-, >NH, >NR³, or an imide group formed by taking together both Y and Y' groups and forming a R¹-N< group between two >C=O groups;

X is independently -Z-O-Z'-, >CH₂, >CHR⁴, >CR⁴R⁵, >C(OH)(CO₂R²), >C(CO₂R²)₂, or >CHOR⁶;

Z and Z' are independently >CH₂, >CHR⁴, >CR⁴R⁵, >C(OH)(CO₂R²), or >CHOR⁶;

n is 0 to 10, with the proviso that when n=1, X is not >CH₂, and when n=2, both X's are not >CH₂;

m is 0 or 1;

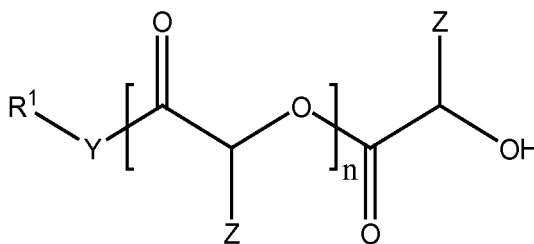
R¹ is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms, with the proviso that when R¹ is hydrogen, m is 0, and n is more than or equal to 1;

R² is a hydrocarbyl group, typically containing 1 to 150 carbon atoms;

R³, R⁴ and R⁵ are independently hydrocarbyl groups; and

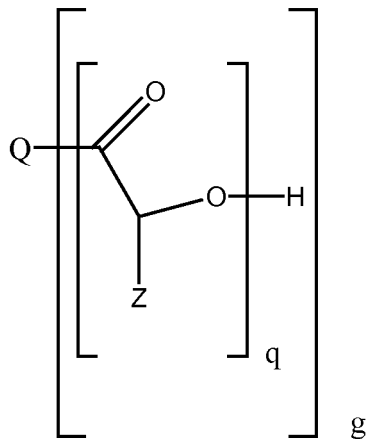
R⁶ is hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms.

[0206] In one embodiment an engine oil lubricant composition comprising the quaternary ammonium salts of the present technology further comprises 0.01 to 5 wt % or 0.1 to 2 wt % of an ashless antiwear agent that may be a compound obtained/obtainable by a process comprising reacting a glycolic acid, a 2-halo-acetic acid, or a lactic acid, or an alkali or alkaline metal salt thereof, (typically glycolic acid or a 2-halo-acetic acid) with at least one member selected from the group consisting of an amine, an alcohol, and an aminoalcohol. For example the compound may be represented by formulae:

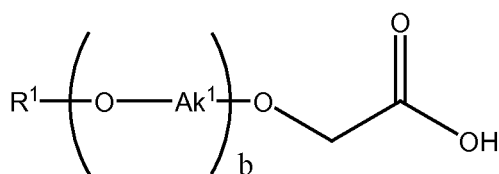


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or



5 or



wherein

- 10 Y is independently oxygen or >NH or >NR¹;
 R¹ is independently a hydrocarbyl group, typically containing 4 to 30, or 6 to 20, or 8 to 18 carbon atoms;
 Z is hydrogen or methyl;
 Q is the residue of a diol, triol or higher polyol, a diamine, triamine, or higher polyamine,
 15 or an aminoalcohol (typically Q is a diol, diamine or aminoalcohol)
 g is 2 to 6, or 2 to 3, or 2;
 q is 1 to 4, or 1 to 3 or 1 to 2;
 n is 0 to 10, 0 to 6, 0 to 5, 1 to 4, or 1 to 3; and
 Ak¹ is an alkylene group containing 1 to 5, or 2 to 4 or 2 to 3 (typically ethylene) carbon
 20 atoms; and
 b is 1 to 10, or 2 to 8, or 4 to 6, or 4.

[0207] The compound is known and is described in International publication WO 2011/022317, and also in granted US Patents 8,404,625, 8,530,395, and 8,557,755.

Industrial Application

[0208] In one embodiment the invention is useful in a liquid fuel or an oil of lubricating viscosity in an internal combustion engine. The internal combustion engine may be a gasoline or diesel engine. Exemplary internal combustion engines include, but are not limited to, spark ignition and compression ignition engines; 2-stroke or 4-stroke cycles; liquid fuel supplied via direct injection, indirect injection, port injection and carburetor; common rail and unit injector systems; light (e.g. passenger car) and heavy duty (e.g. commercial truck) engines; and engines fuelled with hydrocarbon and non-hydrocarbon fuels and mixtures thereof. The engines may be part of integrated emissions systems incorporating such elements as; EGR systems; aftertreatment including three-way catalyst, oxidation catalyst, NO_x absorbers and catalysts, catalyzed and non-catalyzed particulate traps optionally employing fuel-borne catalyst; variable valve timing; and injection timing and rate shaping.

[0209] In one embodiment, the technology may be used with diesel engines having direct fuel injection systems wherein the fuel is injected directly into the engine's combustion chamber. The ignition pressures may be greater than 1000 bar and, in one embodiment, the ignition pressure may be greater than 1350 bar. Accordingly, in another embodiment, the direct fuel injection system maybe a high-pressure direct fuel injection system having ignition pressures greater than 1350 bar. Exemplary types of high-pressure direct fuel injection systems include, but are not limited to, unit direct injection (or "pump and nozzle") systems, and common rail systems. In unit direct injection systems the high-pressure fuel pump, fuel metering system and fuel injector are combined into one apparatus. Common rail systems have a series of injectors connected to the same pressure accumulator, or rail. The rail in turn, is connected to a high-pressure fuel pump. In yet another embodiment, the unit direct injection or common rail systems may further comprise an optional turbocharged or supercharged direct injection system.

[0210] In a further embodiment, the technology is useful for providing at least equivalent, if not improved detergency performance in both the traditional and modern diesel engine compared to a 1000 M_n quaternary ammonium compound. In addition, the technology can provide improved shedding performance compared to 1000 M_n quaternary ammonium compounds in both the traditional and modern diesel engine. In yet another

embodiment, the disclosed technology may be used to improve the cold temperature operability or performance of a diesel fuel (as measured by the ARAL test).

[0211] In yet another embodiment, the invention is useful for lubricating an internal combustion engine (for crankcase lubrication).

5 [0212] Embodiments of the present technology may provide at least one of antiwear performance, friction modification (particularly for enhancing fuel economy), detergent performance (particularly deposit control or varnish control, dispersancy (particularly soot control or sludge control, and corrosion control).

Deposit Control

10 [0213] As fuel burns inside an engine, solid carbonaceous by-products may be produced. The solid by-products may stick to the interior walls of the engine and are often referred to as deposits. If left unchecked, engines fouled by deposits may experience a loss in engine power, fuel efficiency, or drivability.

15 [0214] In traditional diesel engines operating at low pressures (i.e., <35 MPa), deposits form on the fuel injector tips and in the spray holes. These injector tip deposits can disrupt the spray pattern of the fuel, potentially causing a reduction in power and fuel economy. Deposits may also form inside the injectors in addition to forming on the tips. These internal deposits are commonly called internal diesel injector deposits (IDIDs). It is believed that IDIDs have a minor impact, if any on the operation of traditional diesel
20 engines operating at low pressures.

[0215] With the introduction of diesel engines equipped with high pressure common rail fuel injector systems (i.e., >35MPa), however, IDIDs may be more problematic than in traditional diesel engines. In high pressure common rail fuel injector systems, IDIDs can form on injector moving parts, such as the needle and command piston or control
25 valve. IDIDs can hinder the movement of the injector parts, impairing the injection timing and the quantity of fuel injected. Since modern diesel engines operate on precise multiple injection strategies in order to maximize efficiency and performance of combustion, IDIDs can have a serious adverse effect on engine operation and vehicle drivability.

30 [0216] High pressure common rail fuel injector systems are both more susceptible and more prone to IDID formation. These advanced systems have tighter tolerances due to their extremely high operating pressures. Likewise, in some cases the clearance between

moving parts in the injectors is only a few microns or less. As such, advanced diesel fuel systems are more susceptible to IDIDs. Deposits may be likely to form in these systems because of their higher operating temperatures which can oxidize and decompose the chemically unstable components of the diesel fuel. Another factor that may also contribute to IDID issues in high pressure common rail systems is that these injectors often have lower activation forces making them even more prone to sticking than in high pressure systems. The lower activation forces may also cause some of the fuel to “leak back” into the injectors, which may also contribute to IDID.

[0217] Without limiting this specification to one theory of operation, it is believed that IDIDs are formed from when the hydrophilic-lipophilic balance (HLB) of sparingly soluble contaminants moves to a level where the hydrophilic head group dominates over the lipophilic tail. As the length of the lipophilic tail decreases, the hydrophilic head group begins to dominate. The structure of the tail (branched versus linear) and/or may also affect the solubility of the contaminants. In addition, as the polarity of the head group sparingly soluble contaminants increase, its solubility decreases. While there may be multiple causes and sources of IDID, two types of IDIDs have been identified; 1) metal (sodium) carboxylate-type IDIDs, often referred to as “metal soaps” or “sodium soaps”, and 2) amide-type IDIDs, often referred to as “amide lacquers”.

[0218] Advanced chemical analysis techniques have been used to obtain more detailed structural information on IDIDs to help identify the sources of the problem. Detailed analysis of metal soap-type IDIDs has helped identify corrosion inhibitors, such as alkenyl succinic acids, as culprits in IDID formation. The corrosion inhibitors, for example, dodecenyl succinic acid (DDSA) and hexadecenyl succinic acid (HDSA) (two commonly used pipeline corrosion inhibitors in the petroleum industry), pick up trace levels of sodium and other metals in the fuel left over from the refinery process. Tests have been conducted using engines compliant with US Tier 3 emission standards to explore the underlying structure activity relationships of sodium soap formation. Without limiting this specification to one theory of operation, it is believed that the formation of metal soap IDIDs is dependent upon the size (number of carbons) of the hydrocarbon tail of the “soap” and the number of carboxylic acids groups (CO_2H) in the head group of the corrosion inhibitor. It was observed that the tendency to form deposits increases when the inhibitor had a short tail and multiple carboxylic acids in the head group. In other words,

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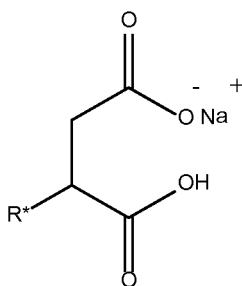
dicarboxylic acid corrosion inhibitors with a lower number average molecular weight (M_n) ranging between 280 and 340, have a greater tendency to form sodium soap deposits than corrosion inhibitors with a higher number average molecular weight. Persons of ordinary skill in the art will understand that there may be some low molecular weight polymers present in corrosion inhibitors with a number average molecular weight above 340.

[0219] These laboratory tests have also shown that deposits can form with as little as 0.5 to 1 ppm of sodium in the fuel along with 8 to 12 ppm of a corrosion inhibitor, such as DDSA or HDSA, and it is possible that real world concentrations may be lower with deposits occurring over longer periods of time, such as 0.01 to 0.5 ppm metal with 1 to 8 ppm corrosion inhibitor.

[0220] These metal soaps can be referred to as low molecular weight soaps, and can be represented, for example, by structures of:



wherein R^* is a linear, branched or cyclic hydrocarbyl group having 10 to 36 carbon atoms, or 12 to 18, or 12 to 16 carbon atoms, M^+ is a metal contaminant, such as sodium, calcium, or potassium, and x is an integer from 1 to 4, 2 to 3, or 2. One class of low molecular weight soaps are those represented by formula:



wherein R^* is defined as above. Particular soaps include DDSA or HDSA soaps. These low molecular weight soaps may have a number average molecular weight (M_n) ranging between 280 and 340.

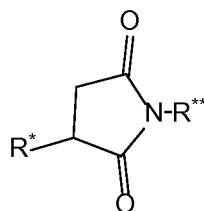
[0221] Amide lacquer formation is less certain but it has been suggested that it is derived from polyisobutylene succinimides (PIBSIs) with low number average molecular weight (M_n) which are added to diesel fuel to control nozzle fouling. Low molecular

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weight PIBSIs may have an average M_n of 400 or less using gel permeation chromatography (GPC) and a polystyrene calibration curve. Alternatively, low M_n PIBSIs may have an average M_n of 200 to 300. These low molecular weight PIBSIs may be byproducts formed from low molecular weight PIBS present in the production process.

5 While generally higher molecular weight polyisobutylene (PIB) with an average M_n of 1000 is used to generate the PIBSIs, low molecular weight PIBs may be present as contaminants. Low molecular weight PIBSIs may also form when increasing the reaction temperature to remove excess reactants or catalysts. Again, while completely eliminating low M_n PIBSIs from anti-foulants might result in reducing IDID formation, complete
10 elimination might not be practical. Accordingly, low M_n PIBSIs may be present in an amount of 5 wt% or less of a total weight of the PIBIs used. It is hypothesized, without limiting this specification to one theory of operation, that the low molecular weight portion of the PIBSI is responsible for deposit formation as it is only sparingly soluble in diesel and thus deposits on the injector surface. In fact, amide lacquer IDIDs have been shown
15 to be linked to low molecular weight species by demonstrating that amide lacquer IDIDs can be produced in US Tier 3-compliant engines using a low molecular weight PIBSI fraction. Here again, laboratory tests have shown that as little as 5 ppm of the low molecular weight PIBSI can cause deposit issues and it is possible that real world concentrations may be lower with deposits occurring over longer periods of time, such as
20 from 0.01 to 5 ppm low molecular weight PIBSI.

[0222] Such low molecular weight PIBSI fractions can be represented, for example, by structure:



25 wherein R^* is as defined above, and R^{**} is a hydrocarbyl polyamine such as an ethylene polyamine.

[0223] The degree of bismaleation of the low molecular weight PIBSI may also affect the polarity of the head group, thereby reducing the PIBSI's solubility in the fuel.

[0224] Another factor that may contribute to IDID formation is the change in diesel fuel to sulfur-free diesel fuel. Sulfur-free diesel fuel is produced by hydrotreating wherein polyaromatics are reduced, thereby lowering the boiling point of the final fuel. As the final fuel is less aromatic, it is also less polar and therefore less able to solubilize sparingly soluble contaminants such as metal soaps or amide lacquers.

[0225] The formation of IDIDs can be reduced in a fuel containing low molecular weight soaps or low molecular weight PIBSI fractions by adding to the fuel the high M_n amide/ester quats with a number average molecular weight ranging from 1300 to 3000 described herein. Thus, an embodiment of the present technology includes fuel compositions comprising at least one low molecular weight soap and the high M_n amide/ester quat as described above.

[0226] In another embodiment, a method of reducing and/or preventing internal diesel injector deposits is disclosed. The method may comprise employing a fuel composition comprising the high M_n amide/ester quat as described above. The fuel may have a low molecular weight soap present therein. In an embodiment, the low molecular weight soap can be derived from the presence of from 0.01 to 5 ppm of a metal and 1 to 12, or 1 to 8, or 8 to 12 ppm of a corrosion inhibitor. Exemplary metals include, but are not limited to, sodium, calcium, and potassium. The corrosion inhibitors may comprise an alkenyl succinic acid such as dodecenyl succinic acid (DDSA) or hexadecenyl succinic acid (HDSA). In yet another embodiment of the present technology the fuel composition may have a low molecular weight polyisobutylene succinimides (PIBSI) present therein. The low molecular weight PIBSI may be present in the fuel at greater than 0.01 ppm, such as, for example, 5 to 25 ppm, or from 0.01 to 5 ppm of a low molecular weight PIBSI.

[0227] In a further embodiment, the technology may include a method of cleaning-up deposits in a diesel engine, such as, a diesel engine having a high pressure (i.e., above 35MPa) common rail injector system, by operating the engine with a fuel containing a high M_n amide/ester quat therein. In an embodiment, the clean-up method includes reducing and/or preventing IDID causing deposits derived from the presence of a low molecular weight soap. In an embodiment, the clean-up method includes reducing and/or preventing IDID causing deposits derived from the presence of a low molecular weight PIBSI.

[0228] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it

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refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, 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); 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); 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. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0229] 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. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the 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 the composition prepared by admixing the components described above.

EXAMPLES

[0230] The invention will be further illustrated by the following examples, which sets forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

Example 1 - Formation of 2300 M_n Polyisobutylene Succinic Anhydride (PIBSA)

[0231] A 2300 number average molecular weight (M_n) polyisobutylene (PIB) (2000 g., 0.80 moles) having greater than 70 % vinylidene groups (high-vinylidene PIB) is charged to a 5-liter flange flask equipped with overhead stirrer, air condenser, nitrogen inlet, thermocouple and Eurotherm™ temperature controller (reaction kit).

[0232] Maleic anhydride (165.5 g, 1.70 moles) is then charged to the reaction vessel. The batch is agitated under a nitrogen blanket and slowly heated to 203 °C over a 90 minute period. The batch is maintained at 203 °C for 24 hours.

[0233] The reaction kit is then reconfigured for vacuum stripping. The batch is stripped at 203 °C and 0.05 bar to remove unreacted maleic anhydride. Diluent oil, such as mineral oil (1116.8 g), is added to the batch. The batch comprising the formed PIBSA is then cooled back to 50 °C and decanted into a storage vessel.

Example 2 (prophetic) - Formation of Quaternizable Compound - 2300 M_n PIBSA and dimethylaminoethanol (DMAE)

[0234] A 2300 M_n PIBSA (1101 g, 0.88 moles, as prepared in Example 1) is charged to a 2-liter flask equipped with a water condenser, a thermocouple, a dropping funnel, an overhead stirrer, and nitrogen inlet and heated to 90 °C.

[0235] DMAE (78.3 g, 0.88 moles) is added to the flask via the dropping funnel over 1 hour while keeping the temperature below 120 °C. Once all the DMAE is added, the reaction is slowly heated to 120 °C and maintained at that temperature for 2 hours. The resulting product is a quaternizable compound comprising 2300 M_n PIBSA/DMAE.

Example 3 (prophetic) - Formation of a 2300 M_n PIBSA/DMAE Quaternary Ammonium Salt using propylene oxide (a DMAE/propylene oxide quat)

[0236] The 2300 M_n PIBSA/DMAE quaternizable compound of Example 2 (380 g, 0.282 moles) and 2-ethylhexanol (110.6 g) are added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet. The reactants are mixed (~180 rpm) and heated to 75 °C.

[0237] Once at temperature, water (3.8g, 0.21 moles) is added to the flask and the reactants are mixed for 30 minutes. Propylene oxide (41.11 g, 0.709 moles) are added subsurface via a syringe pump over 3.5 hours. The batch is then held at 75 °C under

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agitation and nitrogen and maintained at temperature for 3 hours. The DMAE/propylene oxide quat is then then cooled before it is transferred into a storage vessel.

Example 4 - Formation of Quaternizable Compound - 2300 M_n PIBSA and dimethylamino-1-propanol (DMAP)

5 [0238] A 2300 M_n PIBSA (1100 g, 0.88 moles, as prepared in Example 1) is charged to a 2-liter flask equipped with a water condenser, a thermocouple, a dropping funnel, an overhead stirrer and nitrogen inlet and heated to 90 °C.

[0239] DMAP (90.8 g, 0.88 moles) is added to the flask via the dropping funnel over 1 hour while keeping the temperature below 120 °C. Once all the DMAP is added, the
10 reaction is slowly heated to 120 °C and maintained at that temperature for 2 hours. The resulting product is a quaternizable compound comprising 2300 M_n PIBSA/DMAP.

Example 5 (prophetic) - Formation of a 2300 M_n PIBSA/DMAP Quaternary Ammonium Salt Using Propylene Oxide (a DMAP/propylene oxide quat)

15 [0240] The 2300 M_n PIBSA/DMAP quaternizable compound of Example 2 (379.8 g, 0.282 moles) and 2-ethylhexanol (110.7 g) are added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet. The reactants are mixed (~180 rpm) and heated to 75 °C.

[0241] Once at temperature, water (3.8g, 0.21 moles) is added to the flask and the reactants are mixed for 30 minutes. Propylene oxide (41.1 g, 0.708 moles) are added
20 subsurface via a syringe pump over 3.5 hours. The batch is then held at 75 °C under agitation and nitrogen and maintained at temperature for 3 hours. The DMAP/propylene oxide quat is then then cooled before it is transferred into a storage vessel.

Example 6 (prophetic) - Formation of Quaternizable Compound - 2300 M_n PIBSA and 2-dimethylaminopropylamine (DMAPA) – low temperature

25 [0242] 2300 Mn PIBSA (1101g, 0.88 moles) and heptane (502.1g) are added to a 3-liter flask equipped with a water condenser, a thermocouple, a dropping funnel, an overhead stirrer and Nitrogen inlet.

[0243] The flask is then heated to 45 °C. 2-dimethylaminopropylamine is added to the flask via the dropping funnel over an hour. The batch temperature is kept below 50 °C
30 during the addition of 2-dimethylaminopropylamine and is maintained at that temperature for 60 minutes after the addition is complete.

Example 7 (prophetic) - 2300Mn Quaternary Ammonium Salt Using Propylene Oxide (a DMAPA/propylene oxide quat)

[0244] A 1-liter flange flask is equipped with a thermocouple with Eurotherm™ heating, a 4 blade stirrer, a nitrogen sweep, a condenser and a syringe pump.

5 [0245] A 2300 M_n PIBSA and 2-dimethylaminopropylamine (DMAPA) (380.1g, 0.199 moles, product of Example 6) and 2-ethylhexanol (110.8 g) are charged to the flask, and the reaction heated to 45°C, with stirring (180rpm).

10 [0246] Once at temperature, water (3.8 g, 0.21 moles) is charged and the reaction is mixed for 30 minutes. Propylene oxide (29.2g, 0.50 moles) is charged to the flask subsurface via syringe pump over 3 hours and 10 minutes. After the addition is complete, the reaction is held at 45 °C for 3 hours, prior to cooling and discharging without filtering.

15 [0247] The ranges of the components used may vary based on reaction conditions, including batch size and time. For example, if propylene oxide is used as the quaternizing agent, large batches may require less propylene oxide than small batches because larger amounts of propylene oxide will not evaporate as quickly as smaller amounts. Further, some of the components, such as the protic solvent, water and/or acid are optional. Thus, it is possible to make the high M_n amide/ester quat using parameters outside those disclosed in the examples.

20 [0248] The total amount of quat produced may be measured using electrospray ionization mass spectrometry (ESIMS) and nuclear magnetic resonance (NMR). The total amount of quat produced is the percentage of the quaternizable compound converted to the quaternized ammonium salt and may include both imide and amide quats. Thus, the amount of quaternizable compound converted or amount of quaternized salt produced, may range from 60 to 100%, or from 80 to 90%. The quaternized ammonium salt produced
25 may comprise either all amide containing quaternized ammonium salts or a combination of imide and amide quats. For example, in one embodiment, 90% of the quaternized salt may be converted to a quat. All of the quat produced (100%) may be an amide quat. In another embodiment, the amount of quaternizable compound converted to amide quats may range from 25 to 100%. In another embodiment, the amount of quaternizable
30 compound converted to amide quats may range from 30 to 70%, or 35 to 60%, with the balance including imide quats and/or unconverted quaternizable compound. Likewise, the

amount of quaternizable compound converted may comprise 25 to 75% imide quats, with the balance comprising amide quats and and/or unconverted quaternizable compound.

Demulsification (Water Shedding) Testing

[0249] The demulsification test may be performed to measure the high M_n amide/ester quats' ability to demulsify fuel and water mixtures. The demulsification test is run according to the procedure in ASTM D1094-07 ("Standard Test Method for Water Reaction of Aviation Fuels"). The quaternary ammonium salt is added to room temperature fuel at 60 ppm actives by weight based on a total weight of the fuel. Other commercially available demulsifiers may also be added to the fuel.

[0250] The fuel (80 mL) is then added to a clean, 100 mL-graduated cylinder. A phosphate buffer solution with a pH of 7.0 (20 mL) is then added to the graduated cylinder and the cylinder is stoppered. The cylinder is shaken for 2 minutes at 2 to 3 strokes per second and placed on a flat surface. The volume of the aqueous layer, or water recovery, is then measured at 3, 5, 7, 10, 15, 20, and 30-minute intervals.

Deposit Tests – CEC F-23-01 Procedure for Diesel Engine Injector Nozzle Coking Test

[0251] Deposit tests are performed using Peugeot S.A.'s XUD 9 engine in accordance with the procedure in CEC F-23-01. For the first deposit test, air flow is measured through clean injector nozzles of the XUD 9 engine using an air-flow rig. The engine is then run on a reference fuel (RF79) and cycled through various loads and speeds for a period of 10 hours to simulate driving and allow any formed deposits to accumulate. The air-flow through the nozzles are measured again using the air-flow rig. The percentage of air flow loss (or flow remaining) is then calculated.

[0252] A set of deposit tests are performed using the same steps above, except 10 ppm actives of the high M_n amide/ester quat are added to the reference fuel. A second set of deposit tests are performed using the same steps above, except 30 ppm actives are added to the reference fuel.

IDID Tests - CEC F-98-08 DW10B Procedure for Common Rail Diesel Engine Nozzle Coking Test

[0253] Internal diesel injector deposit (IDID) tests are performed using Peugeot S.A.'s DW10 2.0-liter common rail unit with a maximum injection pressure of 1600 bar and fitted with Euro standard 5 fuel injection equipment supplied by Siemens. The test directly

measures engine power, which decreases as the level of injector fouling or IDID increases. The engine is cycled at high load and high speed in timed increments with “soak” periods between the running cycles. The test directly measures engine power, which decreases as the level of injector fouling or IDID increases. For the first test, the engine is run on a reference fuel (RF79) with a trace amount of a zinc salt.

[0254] A second deposit test is performed using the same steps above, except 35 ppm of the high M_n amide/ester quat is added to the reference fuel in addition to the zinc salt.

[0255] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word “about.” Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0256] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

[0257] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the

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scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

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What we claim:

1. A composition comprising a high number average molecular weight ester or amide containing quaternary ammonium salt ("high M_n amide/ester quat"), wherein the high M_n amide/ester quat comprises the reaction product of:

- 5 a) a quaternizable compound that is the reaction product of:
- (i) a hydrocarbyl-substituted acylating agent, wherein the hydrocarbyl-substituent has a number average molecular weight of 1300 to 3000, and
- (ii) a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with said hydrocarbyl-substituted acylating agent to form an ester or amide, and further having at least one quaternizable amino group; and
- 10 b) a quaternizing agent suitable for converting the quaternizable amino group of the nitrogen containing compound to a quaternary nitrogen.

15 2. The composition of claim 1, wherein the quaternizable amino group is a primary, secondary or tertiary amino group.

20 3. The composition of any previous claim, wherein the hydrocarbyl-substituted acylating agent comprises at least one polyisobutenyl succinic anhydride or polyisobutenyl succinic acid.

25 4. The composition of any previous claim, wherein the reaction of a)(i) with a)(ii) is carried out at a temperature of less than 80 °C.

 5. The composition of any previous claim wherein the nitrogen containing compound excludes dimethylaminopropylamine.

30 6. The composition of any previous claim, wherein the quaternizing agent is chosen from dialkyl sulfates, alkyl halides, hydrocarbyl substituted carbonates, hydrocarbyl epoxides, carboxylates, alkyl esters and mixtures thereof.

 7. The composition of claim 6, wherein the quaternizing agent is a hydrocarbyl epoxide.

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8. The composition of claim 7, wherein the quaternizing agent is a hydrocarbyl epoxide in combination with an acid.

9. The composition of claim 6, wherein the quaternizing agent is an oxalate or terephthalate.

10. The composition of any previous claim wherein the quaternizing agent excludes methyl salicylate.

11. The composition of any previous claim, further comprising at least one other additive.

12. The composition of claim 11, wherein the at least one other additive comprises a detergent, a dispersant, a demulsifier, a lubricity agent, a cold flow improver, an antioxidant, or a mixture thereof.

13. The composition of claim 11, wherein the at least one other additive comprises at least one hydrocarbyl-substituted succinic acid.

14. The composition of claim 11, wherein the at least one other additive comprises at least one hydrocarbyl-substituted quaternary ammonium salt.

15. The composition of claim 11, wherein the at least one other additive comprises at least one detergent/dispersant that is an amphiphilic substance which possess at least one hydrophobic hydrocarbon radical with a number average molecular weight of 100 to 10000 and at least one polar moiety selected from (i) Mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties; (ii) Hydroxyl groups in combination with mono or polyamino groups, at least one nitrogen atoms having basic properties; (v) Polyoxy-C₂ to C₄ alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups; (vii) Moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or (viii) Moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono-or polyamines.

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16. The composition of either of claims 13 through 15, wherein the hydrocarbyl-substituent is a polyisobutylene having a molecular weight of 100 to 5000.

17. The composition of claim 11, wherein the at least one other additive comprises at least one Mannich compound.

18. The composition of any previous claim, further comprising a fuel that is liquid at room temperature.

19. The composition of claim 18, wherein the fuel is gasoline or diesel.

20. The fuel composition of claim 18 or 19 further comprising at least one of a low number average molecular weight soap, a low number average molecular weight polyisobutylene succinimide (PIBSI), or a mixture thereof.

21. The fuel composition of claims 18 through 20, further comprising a low number average molecular weight soap with a number average molecular weight (M_n) of less than 340.

22. The fuel composition of claims 18 through 20, further comprising from 0.01 to 25 ppm of a metal and from 1 to 12 ppm of a corrosion inhibitor.

23. The fuel composition of claim 22, wherein the corrosion inhibitor is an alkenyl succinic acid comprising at least one of dodecenyl succinic acid (DDSA), hexadecenyl succinic acid (HDSA), or mixtures thereof.

24. The fuel composition of claims 18 through 20, wherein the fuel comprises PIBSI with a low number average molecular weight M_n of less than 400.

25. A method of improving water shedding performance of a fuel composition comprising employing a composition comprising the high M_n amide/ester quat according to any claims 1 to 24.

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26. The composition of any of claims 1 to 17, further comprising an oil of lubricating viscosity.

27. A method of operating an internal combustion engine comprising:

a) supplying to said engine:

(i) a fuel, wherein said fuel

1. is liquid at room temperature; and

2. has a composition comprising an amide or ester containing quaternary ammonium salt ("high M_n amide/ester quat") according to any claims 1 to 17, and

b) operating said engine.

28. A method of operating an internal combustion engine comprising:

a) supplying to a crankcase of said engine:

(i) an oil of lubricating viscosity having a composition comprising an amide or ester containing quaternary ammonium salt ("high M_n amide/ester quat") according to any claims 1 to 17, and

b) operating said engine.

29. The method of claim 28 wherein the oil of lubricating viscosity has total sulfated ash of less than 1 wt% and/or a phosphorus content of less than 0.11 wt%.

30. A method of reducing and/or preventing injector deposits comprising:

a) supplying to a fuel injector of said engine:

(i) a fuel, wherein said fuel

1. is liquid at room temperature; and

2. has a composition comprising a high M_n amide/ester quat according to any claims 1 to 17 therein; and

b) operating said engine.

31. The method of claim 30, wherein the deposits comprise a low number average molecular weight soap, a low number average molecular weight polyisobutylene succinimide (PIBSI), or mixtures thereof.

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32. The method of claim 31 wherein the fuel comprises a low number average molecular weight soap with a number average molecular weight (M_n) of less than 340.

5 33. The method of claims 30 through 32 wherein the fuel comprises from 0.01 to 25 ppm of a metal and from 1 to 12 ppm of a corrosion inhibitor.

34. The method of claim 33 wherein the corrosion inhibitor is an alkenyl succinic acid comprising at least one of dodecenyl succinic acid (DDSA), hexadecenyl succinic acid (HDSA), or mixtures thereof.

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35. The method of claim 30, wherein the fuel comprises a PIBSI with a low number average molecular weight M_n of less than 400.

15 36. The method of claims 30 to 36, wherein the fuel is gasoline or diesel.

37. The method of any of claims 27 to 35 wherein the engine comprises a high pressure common rail injector system.

20 38. The use of composition of any of claims 1 to 17 to reduce and/or prevent internal deposits in an engine operated with a fuel, wherein the fuel is gasoline or diesel.

39. The use of claim 38 wherein the engine comprises a high pressure common rail injector system.

25 40. The use of claim 38 or 39 wherein said deposits are internal diesel injector deposits (IDID) deposits.