

POLYESTER QUATERNARY AMMONIUM SALTS

Field of the Invention

[0001] The invention relates to polyester amide quaternary ammonium salts, processes for making them, and their use as additives, including their use in fuels, such as diesel fuel and fuel oils. The invention particularly relates to the use of polyester amide quaternary ammonium salts as detergents in fuels and the methods of making them.

Background of the Invention

[0002] Hydrocarbon fuels generally contain numerous deposit-forming substances. When used in internal combustion engines (ICEs), deposits tend to form on and around constricted areas of the engine which are in contact with the fuel. In automobile engines deposits can build up on engine intake valves leading to progressive restriction of the gaseous fuel mixture flow into the combustion chamber and to valve sticking. There are two general types of inlet valve deposits, heavy deposits and thin deposits. These different types of deposits affect the performance of the fuel and the engine in slightly different ways. Heavy deposits are carbonaceous and oily in appearance. They cause flow restriction past the valves, which in turn reduces the maximum power of the engine, decreasing fuel economy and increasing emissions. Thin deposits tend to cause problems on starting the engine and increasing emissions.

[0003] As engines become more sensitive to deposits, it has become common practice to incorporate a detergent in the fuel composition for the purposes of inhibiting the formation, and facilitating the removal, of engine deposits, thereby improving engine performance and emissions.

[0004] It is known to use certain polyisobutylsuccinimide-derived quaternized PIB/amine and/or amide dispersants/detergents as additives in fuel compositions. Polyisobutylsuccinimides may also be described as polyisobutylene succinimides. These quaternized dispersants/detergents are derived from traditional PIB/amine and/or amide fuel additive compounds that have pendant tertiary amine sites which can be alkylated, i.e. quaternized, by a quaternizing

agent, such as propylene oxide. Examples of these additives are disclosed in U.S. patent application US 2008/0307698.

[0005] However there is a need for additives that provide the benefits described above while also exhibiting improved viscosity profiles and material handling properties. Such improvements would allow for the use of less diluent materials in the concentrates and additive packages generally used in the commercial products that contain these types of fuel additives, and so in the final fuels as well. Less diluent would be required if the viscosity profiles and material handling properties allowed for additive-containing compositions to be transferred and handled (i.e. pumped, poured, mixed, etc) without having to heat the material more than typical and/or without the need of specialized high viscosity equipment. Improved viscosity profiles and material handling properties would allow for reduced use of diluents, saving cost, reducing waste and so and improving the environmental impact of the materials. This would also allow the use of more concentrated additive packages and intermediate compositions, which can be transported more efficiently, again reducing costs and environmental impact.

Summary of the Invention

[0006] The present invention deals with a new class of detergents which offer significant improvements over traditional PIB/amine detergents, including polyisobutylsuccinimide-derived quaternized detergents. A new class of polyester amide quaternized salts have now been discovered. These polyester amide quaternized salts have polyester-based hydrocarbyl groups and provide improved viscosity profiles and material handling properties compared to polyisobutylsuccinimide-derived quaternized detergents and related materials. The polyester amide quaternized salts of the invention provide equivalent detergency and thermal stability performance as other quaternized detergents but also provide the improved viscosity profiles and material handling properties described above.

[0007] The present invention provides a composition comprising a quaternized polyester amide salt which comprises the reaction product of: a polyester amide containing a tertiary amino group; and a

quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate. Any of the quaternizing agents described herein may be used in combination with an acid,
5 for example acetic acid.

[0008] The invention provides for quaternized polyester amide salts where the polyester amide used in their preparation is itself the reaction product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having a nitrogen atom capable of condensing with said acid and further having
10 a tertiary amino group.

[0009] The invention further provides for fuel compositions that include the quaternized polyester amide salts described herein and a fuel which is liquid at room temperature. Additional fuel additives may also be present.

[0010] The invention provides for methods of fueling an internal combustion engine comprising the steps of supplying to the engine a fuel which is liquid at
15 room temperature and a composition comprising one or more of the quaternized polyester amide salts described herein.

[0011] The invention also provides for a process of making a quaternary ammonium salt detergent comprising the steps of reacting (a) a polyester amide containing a tertiary amino group; and (b) a quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate. The described process results in the quaternized dispersants described herein.
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25 **Detailed Description of the Invention**

[0012] Various preferred features and embodiments will be described below by way of non-limiting illustration.

The Polyester Quaternary Ammonium Salt Detergent

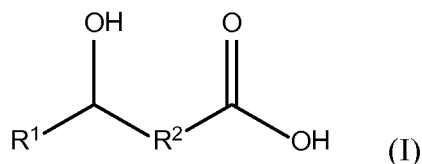
[0013] The polyester quaternary salts detergents of the invention include
30 quaternized polyester amine, amide, and ester salts. The additives may also be described as quaternary polyester salts. The additives of the invention may be

described as the reaction product of: a polyester containing a tertiary amino group; and a quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen. The quaternizing agent may be selected from the group consisting of dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.

a. The Non-Quaternized Polyester

[0014] The polyester containing a tertiary amino group used in the preparation of the additives of the invention may also be described as a non-quaternized polyester containing a tertiary amino group.

[0015] In some embodiments the polyester is the reaction product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group. Suitable fatty carboxylic acids that may be used in the preparation of the polyesters described above may be represented by the formula:

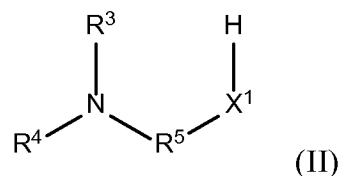


where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms.

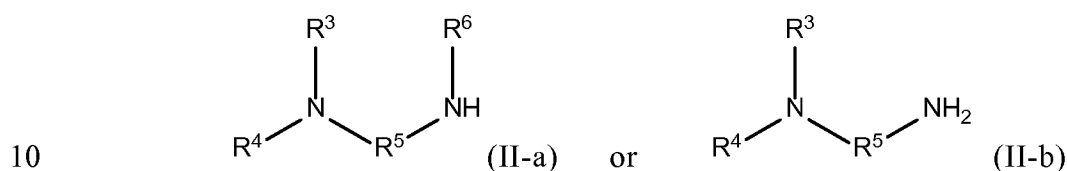
In some embodiments R^1 contains from 1 to 12, 2 to 10, 4 to 8 or even 6 carbon atoms, and R^2 contains from 2 to 16, 6 to 14, 8 to 12, or even 10 carbon atoms.

[0016] In some embodiments the fatty carboxylic acid used in the preparation of the polyester is 12-hydroxystearic acid, ricinoleic acid, 12-hydroxy dodecanoic acid, 5-hydroxy dodecanoic acid, 5-hydroxy decanoic acid, 4-hydroxy decanoic acid, 10-hydroxy undecanoic acid, or combinations thereof.

[0017] In some embodiments the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group is represented by the formula:



where R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene group containing from 1 to 20 carbon atoms; and X^1 is O or NR^6 where R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms. In some embodiments R^3 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^4 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^5 contains from 2 to 12, 2 to 8 or even 3 carbon atoms, and R^6 contains from 1 to 8, or 1 to 4 carbon atoms. In some of these embodiments, formula (II) becomes:



where the various definitions provided above still apply.

[0018] Examples of nitrogen or oxygen containing compounds capable of condensing with the acylating agents, which also have a tertiary amino group, or compounds that can be alkylated into such compounds, include but are not limited to: 1-aminopiperidine, 1-(2-aminoethyl)piperidine, 1-(3-aminopropyl)-2-pipecoline, 1-methyl-(4-methylamino)piperidine, 4-(1-pyrrolidinyl)piperidine, 1-(2-aminoethyl)pyrrolidine, 2-(2-aminoethyl)-1-methylpyrrolidine, N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-diethyl-1,3-diaminopropane, N,N-dimethyl-1,3-diaminopropane, N,N,N'-trimethylethylenediamine, N,N-dimethyl-N'-ethylethylenediamine, N,N-diethyl-N'-methylethylenediamine, N,N,N'-triethylethylenediamine, 3-dimethylaminopropylamine, 3-diethylaminopropylamine, 3-dibutylaminopropylamine, N,N,N'-trimethyl-1,3-propanediamine, N,N,2,2-tetramethyl-1,3-propanediamine, 2-amino-5-diethylaminopentane, N,N,N',N'-tetraethyldiethylenetriamine, 3,3'-diamino-N-methyldipropylamine, 3,3'-iminobis(N,N-dimethylpropylamine), or combinations thereof. In such embodiments, the resulting additive includes a quaternary

ammonium amide salt, that is a detergent containing an amide group and a quaternary ammonium salt.

[0019] The nitrogen or oxygen containing compounds may further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine.

[0020] Another type of nitrogen or oxygen containing compounds capable of condensing with the acylating agent and having a tertiary amino group, in some embodiments after further alkylation, include alkanolamines including but not limited to triethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamino)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanol amine, N-butyldiethanolamine, N,N-diethylaminoethanol, N,N-dimethyl aminoethanol, 2-dimethylamino-2-methyl-1-propanol. In embodiments where alkanolamines and/or similar materials are used, the resulting additive includes a quaternary ammonium ester salt, that is a detergent containing an ester group and a quaternary ammonium salt.

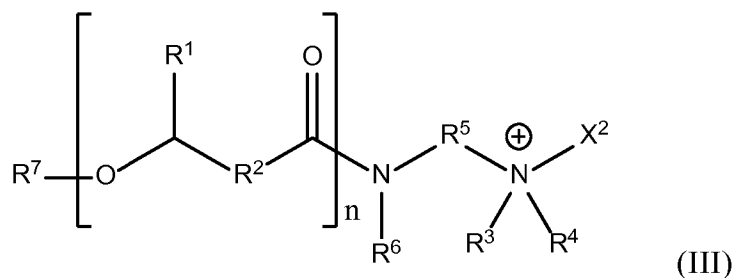
[0021] In one embodiment the nitrogen or oxygen containing compound is triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamino)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanolamine, N-butyldiethanolamine, N,N-diethylaminoethanol, N,N-dimethylaminoethanol, 2-dimethylamino-2-methyl-1-propanol, or combinations thereof.

[0022] In some embodiments the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group comprises N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-dimethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, N,N-dimethylaminoethanol, N,N-diethylaminoethanol, or combinations thereof.

[0023] The quaternized polyester salt can be a quaternized polyester amide salt. In such embodiments the polyester containing a tertiary amino group used to prepare the quaternized polyester salt is a polyester amide containing a tertiary amino group. In some of these embodiments the amine or aminoalcohol is reacted with a monomer and then the resulting material is polymerized with

additional monomer, resulting in the desired polyester amide which may then be quaternized.

[0024] In some embodiments the quaternized polyester salt includes an cation represented by the following formula:



where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; n is a number from 1 to 20 or from 1 to 10; R^7 is hydrogen, a hydrocarbonyl group containing from 1 to 22 carbon atoms, or a hydrocarbyl group containing from 1 to 22 carbon atoms; and X^2 is a group derived from the quaternizing agent. In some embodiments R^6 is hydrogen.

[0025] As above, in some embodiments R^1 contains from 1 to 12, 2 to 10, 4 to 8 or even 6 carbon atoms, and R^2 contains from 1 or even 2 to 16, 6 to 14, 8 to 12, or even 10 carbon atoms, R^3 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^4 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^5 contains from 2 to 12, 2 to 8 or even 3 carbon atoms, and R^6 contains from 1 to 8, or 1 to 4 carbon atoms. In any of these embodiments n may be from 2 to 9, or 3 to 7, and R^7 may contain from 6 to 22, or 8 to 20 carbon atoms. R^7 may be an acyl group.

[0026] In these embodiments the quaternized polyester salt is essentially capped with a C1-22, or a C8-20, fatty acid. Examples of suitable acids include oleic acid, palmitic acid, stearic acid, erucic acid, lauric acid, 2-ethylhexanoic acid, 9,11-linoleic acid, 9,12-linoleic acid, 9,12,15-linolenic acid, abietic acid, or combinations thereof.

[0027] The number average molecular weight (M_n) of the quaternized polyester salts of the invention may be from 500 to 3000, or from 700 to 2500.

[0028] The polyester useful in the present invention can be obtained by heating one or more hydroxycarboxylic acids or a mixture of the hydroxycarboxylic acid and a carboxylic acid, optionally in the presence of an esterification catalyst. The hydroxycarboxylic acids can have the formula HO-X-COOH wherein X is a divalent saturated or unsaturated aliphatic radical containing at least 8 carbon atoms and in which there are at least 4 carbon atoms between the hydroxy and carboxylic acid groups, or from a mixture of such a hydroxycarboxylic acid and a carboxylic acid which is free from hydroxy groups. This reaction can be carried out at a temperature in the region of 160 C to 200 C, until the desired molecular weight has been obtained. The course of the esterification can be followed by measuring the acid value of the product, with the desired polyester, in some embodiments, having an acid value in the range of 10 to 100 mg KOH/g or in the range of 20 to 50 mg KOH/g. The indicated acid value range of 10 to 100 mg KOH/g is equivalent to a number average molecular weight range of 5600 to 560. The water formed in the esterification reaction can be removed from the reaction medium, and this can be conveniently done by passing a stream of nitrogen over the reaction mixture or, by carrying out the reaction in the presence of a solvent, such as toluene or xylene, and distilling off the water as it is formed.

[0029] The resulting polyester can then be isolated in conventional manner; however, when the reaction is carried out in the presence of an organic solvent whose presence would not be harmful in the subsequent application, the resulting solution of the polyester can be used.

[0030] In the said hydroxycarboxylic acids the radical represented by X may contain from 12 to 20 carbon atoms, optionally where there are between 8 and 14 carbon atoms between the carboxylic acid and hydroxy groups. In some embodiments the hydroxy group is a secondary hydroxy group.

[0031] Specific examples of such hydroxycarboxylic acids include ricinoleic acid, a mixture of 9- and 10-hydroxystearic acids (obtained by sulphation of oleic acid followed by hydrolysis), and 12-hydroxystearic acid, and especially

the commercially available hydrogenated castor oil fatty acid which contains in addition to 12-hydroxystearic acid minor amounts of stearic acid and palmitic acid.

5 [0032] The carboxylic acids which can be used in conjunction with the hydroxycarboxylic acids to obtain these polyesters are preferably carboxylic acids of saturated or unsaturated aliphatic compounds, particularly alkyl and alkenyl carboxylic acids containing a chain of from 8 to 20 carbon atoms. As examples of such acids there may be mentioned lauric acid, palmitic acid, stearic acid and oleic acid.

10 [0033] In one embodiment the polyester is derived from commercial 12-hydroxy-stearic acid having a number average molecular weight of about 1600. Polyesters such as this are described in greater detail in U.K. Patent Specification Nos. 1373660 and 1342746.

15 [0034] In some embodiments the components used to prepare the additives described above are substantially free of, essentially free of, or even completely free of, non-polyester-containing hydrocarbyl substituted acylating agents and/or non-polyester-containing hydrocarbyl substituted diacylating agents, such as for example polyisobutylene succinic anhydride. In some embodiments these excluded agents are the reaction product of a long chain hydrocarbon, 20 generally a polyolefin reacted with a monounsaturated carboxylic acid reactant, such as, (i) α,β -monounsaturated C_4 to C_{10} dicarboxylic acid, such as, fumaric acid, itaconic acid, maleic acid.; (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or di-esters of (i); (iii) α,β -monounsaturated C_3 to C_{10} monocarboxylic acid such as acrylic acid and methacrylic acid.; or (iv) 25 derivatives of (iii), such as, C_1 to C_5 alcohol derived esters of (iii) with any compound containing an olefinic bond represented by the general formula $(R^9)(R^{10})C=C(R^{11})(CH(R^7)(R^8))$ wherein each of R^9 and R^{10} is independently hydrogen or a hydrocarbon based group; each of R^{11} , R^7 and R^8 is independently hydrogen or a hydrocarbon based group and preferably at least one is a hydrocarbyl group containing at least 20 carbon atoms. In one embodiment, the 30 excluded hydrocarbyl-substituted acylating agent is a dicarboxylic acylating

agent. In some of these embodiments, the excluded hydrocarbyl-substituted acylating agent is polyisobutylene succinic anhydride.

[0035] By substantially free of, it is meant that the components of the present invention are primarily composed of materials other than hydrocarbyl substituted acylating agents described above such that these agents are not significantly involved in the reaction and the compositions of the invention do not contain significant amounts of additives derived from such agents. In some embodiments the components of the invention, or the compositions of the invention, may contain less than 10 percent by weight of these agents, or of the additives derived from these agents. In other embodiments the maximum allowable amount may be 5, 3, 2, 1 or even 0.5 or 0.1 percent by weight. One of the purposes of these embodiments is to allow the exclusion of agents such as polyisobutylene succinic anhydrides from the reactions of the invention and so, to also allow the exclusion of quaternized salt detergent additive derived from agents such as polyisobutylene succinic anhydrides. The focus of this invention is on polyester, or hyperdispersant, quaternary salt detergent additives.

b. The Quaternizing Agent

[0036] The quaternized salt detergents of the present invention are formed when the non-quaternized detergents described above are reacted with a quaternizing agent. Suitable quaternizing agents include selected dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.

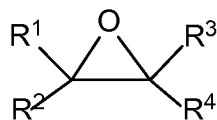
[0037] In one embodiment, the quaternizing agent can include alkyl halides, such as chlorides, iodides or bromides; alkyl sulphonates; dialkyl sulphates, such as, dimethyl sulphate; sultones; alkyl phosphates; such as, C1-12 trialkylphosphates; di C1-12 alkylphosphates; borates; C1-12 alkyl borates; alkyl nitrites; alkyl nitrates; dialkyl carbonates; alkyl alkanoates; O,O-di-C1-12 alkyldithiophosphates; or mixtures thereof.

[0038] In one embodiment, the quaternizing agent may be derived from dialkyl sulphates such as dimethyl sulphate, N-oxides, sultones such as propane and butane sultone; alkyl, acyl or aralkyl 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.

[0039] 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.

[0040] In another embodiment, the quaternizing agent can be a hydrocarbyl epoxide, as represented by the following formula, in combination with an acid:



(VIII)

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.

[0041] In some embodiments the acid used with the hydrocarbyl epoxide may be a separate component, such as acetic acid. In other embodiments, for example when the hydrocarbyl acylating agent is a dicarboxylic acylating agent, no separate acid component is needed. In such embodiments, the detergent may be prepared by combining reactants which are essentially free of, or even free of, a separate acid component, such as acetic acid, and rely on the acid group of the hydrocarbyl acylating agent instead. 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 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.

[0042] In some embodiments the quaternizing agent of the invention does not contain any substituent group that contains more than 20 carbon atoms. In other words, in some embodiments the long substituent group that allows for the resulting additive to be organic soluble and thus useful for the purposes of this

invention is not provided by the quaternizing agent but instead is brought to the additive by the non-quaternized detergents described above.

[0043] In certain embodiments the molar ratio of detergent having an amine functionality to quaternizing agent is 1:0.1 to 2, or 1:1 to 1.5, or 1:1 to 1.3.

- 5 [0044] 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:



- 10 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.

- [0045] 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 may be a substituted aryl group having 6 to 10 carbon atoms, a phenyl group, or a naphthyl group. R 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.

- [0046] 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.

[0047] In some embodiments the quaternizing agent is an ester of an alpha-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 alpha-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.

[0048] In some embodiments the quaternizing agent comprises an ester of a polycarboxylic acid. In this definition we mean to include 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.

[0049] In some embodiments the quaternizing agent is an ester of a carboxylic acid having a pK_a 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, methyl 2-nitrobenzoate and methyl salicylate.

[0050] 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.

Polyester Quaternized Detergent Containing Compositions

[0051] The quaternized salt detergents of the present invention may be used as an additive in various types of compositions, including fuel compositions and additive concentrate compositions.

5 *a. Fuel Compositions*

[0052] The quaternized detergents of the present invention may be used as an additive in fuel compositions. The fuel compositions of the present invention comprise the quaternized detergent additive described above and a liquid fuel, and is useful in fueling an internal combustion engine or an open flame burner.

10 These compositions may also contain one or more additional additives. These optional additives are described below. In some embodiments, the fuels suitable for use in the present invention include any commercially available fuel, and in some embodiments any commercially available diesel fuel and/or biofuel.

[0053] The description that follows of the types of fuels suitable for use in
15 the present invention refer to the fuel that may be present in the additive containing compositions of the present invention as well as the fuel and/or fuel additive concentrate compositions to which the additive containing compositions may be added.

[0054] Fuels suitable for use in the present invention are not overly limited.
20 Generally, suitable fuels are normally liquid at ambient conditions e.g., room temperature (20 to 30°C) or are normally liquid at operating conditions. The fuel can be a hydrocarbon fuel, non-hydrocarbon fuel, or mixture thereof.

[0055] The hydrocarbon fuel can be a petroleum distillate, including a gasoline as defined by ASTM specification D4814, or a diesel fuel, as defined
25 by ASTM specification D975. In one embodiment the liquid fuel is a gasoline, and in another embodiment the liquid fuel is a non-leaded gasoline. In another embodiment the liquid 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, and option-
30 ally hydro-isomerized. In some embodiments, the fuel used in the present invention is a diesel fuel, a biodiesel fuel, or combinations thereof.

[0056] Suitable fuels also include heavier fuel oils, such as number 5 and number 6 fuel oils, which are also referred to as residual fuel oils, heavy fuel oils, and/or furnace fuel oils. Such fuels may be used alone or mixed with other, typically lighter, fuels to form mixtures with lower viscosities. Bunker fuels are also included, which are generally used in marine engines. These types of fuels have high viscosities and may be solids at ambient conditions, but are liquid when heated and supplied to the engine or burner it is fueling.

[0057] The non-hydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, which includes alcohols, ethers, ketones, esters of a carboxylic acids, nitroalkanes, or mixtures thereof. Non-hydrocarbon fuels can include 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.

[0058] Mixtures of hydrocarbon and non-hydrocarbon 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 and other bio-derived fuels. In one embodiment the liquid fuel is an emulsion of water in a hydrocarbon fuel, a non-hydrocarbon fuel, or a mixture thereof.

[0059] In several embodiments of this invention the liquid fuel can have a sulphur content on a weight basis that is 50,000 ppm or less, 5000 ppm or less, 1000 ppm or less, 350 ppm or less, 100 ppm or less, 50 ppm or less, or 15 ppm or less.

[0060] The liquid fuel of the invention is present in a fuel composition in a major amount that is generally greater than 95% by weight, and in other embodiments is present at greater than 97% by weight, greater than 99.5% by weight, greater than 99.9% by weight, or greater than 99.99% by weight.

b. Additive Concentrate Compositions

[0061] Additive concentrates are compositions that contain one or more additives and which may also contain some amount of fuel, oil, or a diluent of some type. These concentrates can then be added to other compositions as a convenient way to handle and deliver the additives, resulting in the final compositions such as the fuel compositions described above.

[0062] The additive concentrate compositions of the present invention contain one or more of the quaternized detergents described above and an optional diluent, which may be any of the fuels described above, a solvent, a diluent oil, or similar material. These compositions may also contain one or more of the additional additives described below.

c. Optional Additional Additives

[0063] The compositions of the present invention include the quaternized detergents 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.

[0064] Although any of the additional performance additives described herein can be used in any of the compositions of the invention, the following additional additives are particularly useful for fuel 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.

[0065] 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 demulsifiers include for example polyalkoxylated alcohols. Suitable lubricity agents include for example fatty carboxylic acids. Suitable metal deactivators include for example aromatic triazoles or derivatives thereof, including but not limited to benzotria-

zole. 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-trifluoropropylmethyl 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.

[0066] The additional performance additives, which may be present in the compositions of the invention, also include di-ester, di-amide, ester-amide, and ester-imide friction modifiers prepared by reacting a dicarboxylic acid (such as tartaric acid) and/or a 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.

[0067] The additional performance additives may comprise a high TBN nitrogen containing detergent/dispersant, such as a succinimide, that is the condensation product of 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. 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. Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy charac-

teristics 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.

[0068] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptotriadiazoles, 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.

[0069] The compositions of the invention may include a detergent additive, different from the quaternized salt additive of the invention. 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 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.

[0070] 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.

[0071] Antioxidants encompass phenolic antioxidants, which may comprise a butyl substituted phenol containing 2 or 3 t-butyl groups. The para position may also be occupied by a hydrocarbonyl group or a group bridging two aromatic rings. The latter antioxidants are described in greater detail in U.S. Patent 6,559,105. Antioxidants also include aromatic amines, such as nonylated diphenylamine. Other antioxidants include sulfurized olefins, titanium compounds, and molybdenum compounds. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition. Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5, or 0.15 to 4.5, or 0.2 to 4 percent by weight. Additionally, more than one antioxidant may be present, and certain combinations of these can be synergistic in their combined overall effect.

[0072] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the 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.

[0073] Multifunctional viscosity improvers, which also have dispersant and/or antioxidant properties are known and may optionally be used. 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.

[0074] 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 compositions of the invention are free of phosphorus-containing antiwear/extreme pressure agents.

[0075] Any of the additional performance additives described above may be added to the compositions of the present invention. Each may be added directly to the additive and/or the compositions of the present invention, but they are generally mixed with the additive to form an additive composition, or concentrate, which is then mixed with fuel to result in a fuel composition. These various types of compositions are described in more detail above. The amount of additional additives in the present composition can typically be 1 to 10 weight percent, or 1.5 to 9.0 percent, or 2.0 to 8.0 percent, all expressed on an oil-free basis.

The Process of Preparing the Quaternized Salt Detergent

[0076] The present invention provides a process of preparing quaternized amide and/or ester detergent where the process includes: reacting (a) a polyester containing a tertiary amino group; and (b) quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen, thereby obtaining the quaternized dispersant.

[0077] As described above the quaternizing agent may be selected from the group consisting of dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.

[0078] The processes of the present invention may also be described as a process for preparing a quaternized detergent comprising the steps of: (1) mixing (a) a polyester containing a tertiary amino group, (b) a quaternizing agent and optionally (c) a protic solvent; (2) heating the mixture to a temperature between 50°C to 130°C; and (3) holding for the reaction to complete; thereby obtaining the quaternized detergent. In one embodiment the reaction is carried out at a temperature of less than 80°C, or less than 70°C. In other embodiments the reaction mixture is heated to a temperature of about 50°C to 120°C, 80°C, or 70°C. In still other embodiments the reaction temperature may be 70°C to 130°C. In other embodiments the reaction temperature may be 50°C to 80°C or 50°C to 70°C.

[0079] In some embodiments the processes of the present invention are free of the addition of any acid reactant, such as acetic acid. The salt product is obtained in these embodiments despite the absence of the separate acid reactant.

[0080] As described above, in some embodiments the non-quaternized polyester containing a tertiary amino group is the condensation product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group, thereby obtaining the polyester containing a tertiary amino group. In some embodiments the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a

tertiary amino group is a diamine containing a tertiary amino group and a primary or secondary amino group.

[0081] The additives of the present invention may be derived in the presence of a protic solvent. Suitable protic solvents include solvents that have dielectric constants of greater than 9. In one embodiment the protic solvent includes compounds that contain 1 or more hydroxyl (-OH) functional groups, and may include water.

[0082] In one embodiment, the solvents are glycols and glycol ethers. Glycols containing from 2 to 12 carbon atoms, or from 4 to 10, or 6 to 8 carbon atoms, and oligomers thereof (e.g., dimers, trimers and tetramers) are generally suitable for use. Illustrative glycols include ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, triethylene glycol, polyethylene glycol and the like and oligomers and polymeric derivative and mixtures thereof. Illustrative glycol ethers include the C₁-C₆ alkyl ethers of propylene glycol, ethylene glycol and oligomers thereof such as di-, tri- and tetra glycol ethers of methyl, ethyl, propyl, butyl or hexyl. Suitable glycol ethers include ethers of dipropylene glycol, tripropylene glycol diethylene glycol, triethylene glycol; ethyl diglycol ether, butyl diethyleneglycol ether, methoxytriethyleneglycol, ethoxytriethyleneglycol, butoxytriethyleneglycol, methoxytetraethyleneglycol, butoxytetraethyleneglycol.

[0083] Suitable solvents for use in the invention also include alcohols from C₁-C₂₀ including branched hydrocarbyl alcohols. Examples of suitable alcohols include 2-methylheptanol, 2-methyldecanol, 2-ethylpentanol, 2-ethylhexanol, 2-ethylnonanol, 2-propylheptanol, 2-butylheptanol, 2-butyloctanol, isooctanol, dodecanol, cyclohexanol, methanol, ethanol, propan-1-ol, 2-methylpropan-2-ol, 2-methylpropan-1-ol, butan-1-ol, butan-2-ol, pentanol and its isomers, and mixtures thereof. In one embodiment the solvent of the present invention is 2-ethylhexanol, 2-ethyl nonanol, 2-propylheptanol, or combinations thereof. In one embodiment the solvent of the present invention includes 2-ethylhexanol.

[0084] The solvent can be any of the commercially available alcohols or mixtures of such alcohols and also includes such alcohols and mixtures of

alcohols mixed with water. In some embodiments water is the only solvent used. In some embodiments the amount of water present may be above 1 percent by weight of the solvent mixture. In other embodiments the solvent mixture may contain traces of water, with the water content being less than 1 or 0.5 percent by weight.

[0085] The alcohols can be aliphatic, cycloaliphatic, aromatic, or heterocyclic, including aliphatic-substituted cycloaliphatic alcohols, aliphatic-substituted aromatic alcohols, aliphatic-substituted heterocyclic alcohols, cycloaliphatic-substituted aliphatic alcohols, cycloaliphatic-substituted aromatic alcohols, cycloaliphatic-substituted heterocyclic alcohols, heterocyclic-substituted aliphatic alcohols, heterocyclic-substituted cycloaliphatic alcohols, and heterocyclic-substituted aromatic alcohols.

[0086] While not wishing to be bound by theory, it is believed that a polar protic solvent (which may include water) is required in order to facilitate the dissociation of the acid into ions and protons. The dissociation is required to protonate the ion formed when the detergent having an amine functionality initially reacts with the quaternizing agent. In the case where the quaternizing agent is an alkyl epoxide the resulting ion would be an unstable alkoxide ion. The dissociation also provides a counter ion from the acid group of the additive that acts to stabilize the quaternary ammonium ion formed in the reaction, resulting in a more stable product.

Industrial Application

[0087] In one embodiment, the process of the present invention produces a quaternized salt detergent. The quaternized detergent can be used as an additive for use in a fuel for use in an internal combustion engine and/or an open flame burner.

[0088] The internal combustion engine includes 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.

5 **[0089]** The open flame burner burning may be any open-flame burning apparatus equipped to burn a liquid fuel. These include domestic, commercial and industrial burners. The industrial burners include those requiring preheating for proper handling and atomization of the fuel. Also included are oil fired combustion units, oil fired power plants, fired heaters and boilers, and boilers
10 for use in ships and marine applications including deep draft vessels. Included are boilers for power plants, utility plants, and large stationary and marine engines. The open-flame fuel burning apparatus may be an incinerator such as rotary kiln incinerator, liquid injection kiln, fluidized bed kiln, cement kiln, and the like. Also included are steel and aluminum forging furnaces. The open-
15 flame burning apparatus may be equipped with a flue gas recirculation system.

[0090] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydro-
20 carbyl 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,
25 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
30 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. As used herein, the term “hydrocarbonyl group” or “hydrocarbonyl substituent” means a hydrocarbyl group containing a carbonyl group.

- 5 [0091] 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
10 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

- 15 [0092] The invention will be further illustrated by the following examples. While the Examples are provided to illustrate the invention, they are not intended to limit it.

Example A – Non-Quaternized Polyester Amide (preparatory material)

- [0100] A non-quaternized polyester amide is prepared by reacting, in a jacketed
20 reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 6 moles of 12-hydroxystearic acid and 1 mole of dimethylaminopropylamine where the reaction is carried out at about 130°C and held for about 4 hours. The reaction mixture is then cooled to about 100°C and zirconium butoxide is added, in an amount
25 so that the catalyst makes up 0.57 percent by weight of the reaction mixture. The reaction mixture is heated to about 195°C and held for about 12 hours. The resulting product is cooled and collected.

Example B – Quaternized Polyester Amide Salt Detergent (inventive example)

- [0101] A quaternized polyester amide salt detergent is prepared by reacting, in a
30 jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 600 grams of the non-quaternized polyester amide of Example A, 120 grams

of 2-ethylhexanol, 18.5 grams of acetic acid, and 32.3 ml of propylene oxide, where the reaction is carried out at about 75°C and the propylene oxide is fed in to the reaction vessel over about 3.5 hours. The reaction mixture is then held at temperature for about 3 hours. 760 grams of product is cooled and collected, which TAN, FTIR and ESI-MS analysis confirms to be about 80% by weight quaternized polyester amide salt detergent, with the remaining material being primarily non-quaternized polyester amide. The collected material has a TAN of 1.26 mg KOH/gram, a TBN of 23.82 mg KOH/gram, a kinematic viscosity at 100°C of 28.58 cSt (as measured by ASTM D445), an acetate peak by IR at 1574 cm⁻¹, and is 1.22% nitrogen.

10 Example C – Non-Quaternized Polyester Amide (preparatory material)

[0102] A non-quaternized polyester amide is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 1300 grams of ricinoleic acid and 73.5 grams of dimethylaminopropylamine where the reaction is carried out at about 130°C, the amine is added dropwise over about 8 minutes, and the reaction mixture held for about 4 hours. The reaction mixture is then cooled to about 100°C and 7.8 grams of zirconium butoxide is added. The reaction mixture is heated to about 195°C and held for about 17 hours. The resulting product is filtered, cooled and collected. 1301 grams of product is collected which has a TAN of 0 mg KOH/gram and shows by IR an ester peak at 1732 cm⁻¹, an amide peak at 1654 cm⁻¹, but no acid peak at 1700 cm⁻¹.

Example D – Quaternized Polyester Amide Salt Detergent (inventive example)

[0103] A quaternized polyester amide salt detergent is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 600 grams of the non-quaternized polyester amide of Example C, 123 grams of 2-ethylhexanol, 18.9 grams of acetic acid, and 33.1 ml of propylene oxide, where the reaction is carried out at about 75°C and the propylene oxide is fed in to the reaction vessel over about 3.5 hours. The reaction mixture is then held at temperature for about 3 hours. 751 grams of product is cooled and collected, which TAN, FTIR and ESI-MS analysis confirms to be about 70% by weight quaternized polyester amide salt detergent, with the remaining material being primarily non-quaternized

polyester amide. The collected material has a TAN of 0 mg KOH/gram, a TBN of 23.14 mg KOH/gram, a kinematic viscosity at 100°C of 47.0 cSt (as measured by ASTM D445), an acetate peak by IR at 1574 cm⁻¹.

Example E – Non-Quaternized Polyisobutylene Detergent (comparative example)

5 **[0104]** A non-quaternized polyisobutylene monosuccinimide detergent is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 100 pbw polyisobutylene succinic anhydride (which is itself prepared from 1000 number average molecular weight high vinylidene polyisobutylene and maleic anhydride reaction in a 1:1.2 molar ratio) 13 pbw tetraethylenepentamine, where the anhydride is preheated to about 80°C, the amine is added to the system over about 8 hours, where the reaction mixture temperature is kept below 120°C. The reaction mixture is then heated to 170°C and then vacuum stripped. The resulting non-quaternized polyisobutylene monosuccinimide detergent is cooled and collected.

Example F – Quaternized Polyisobutylene Detergent (comparative example)

20 **[0105]** A quaternized polyisobutylene succinimide detergent is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 100 pbw polyisobutylene succinic anhydride (which is itself prepared from 1000 number average molecular weight high vinylidene polyisobutylene and maleic anhydride reaction in a 1:1.2 molar ratio) 10.9 pbw dimethylaminopropylamine, where the anhydride is preheated to about 80°C, the amine is added to the system over about 8 hours, where the reaction mixture temperature is kept below 120°C. The reaction mixture is then heated to 150°C and held for 3 hours, resulting in a non-quaternized polyisobutylene succinimide detergent. 40.6 pbw 2-ethylhexanol, 1 pbw water, 5.9 pbw acetic acid is then added to the non-quaternized polyisobutylene succinimide detergent. After a 3 hour hold 8.5 pbw propylene oxide is added with the reaction being held at 75°C for about 6 hours. The resulting quaternized polyisobutylene succinimide detergent is cooled and collected.

XUD-9 Engine Testing

[0106] The Peugeot XUD-9 engine in an indirect injection engine. In the test the percent flow remaining in the fuel injector is measured at the end of the test, with higher percent flow remaining being desired, as indicative of reduced injector deposit formation. Separate XUD-9 engine tests were performed on a fuel composition containing Example B, a fuel composition containing Example F, and a fuel composition contain Example E. Each composition uses the same base fuel and contains 71 ppm of the additive being evaluated. The base fuel is known to give a percent remaining flow of less than 20% when tested alone. The results obtained are as follows:

10 *Table 1 – XUD-9 Engine Test Results*

Fuel Sample	Additive Evaluated	Percent Flow Remaining
1	Inventive Example B	84
2	Comparative Example F	100
3	Comparative Example E	36

[0107] The results show that the Inventive Example B additive performs about as well as the quaternized polyisobutylene succinimide detergent of Example F and much better than the non-quaternized polyisobutylene succinimide detergent of Example E. All of the examples perform better than the base fuel alone, however the additives of Examples B and F perform significantly better than the base fuel.

[0108] As discussed herein, the comparable XUD-9 engine test performance delivered by Inventive Example B and Comparative Example F is important when one then considers the superior viscosity and materials handling properties of Inventive Example B, further demonstrated below.

DW-10 Engine Testing

[0109] The DW-10 screen test uses the Coordinating European Council's (CEC) F-98-08 testing protocol, which utilizes a Peugeot DW-10 engine. This is a light duty direct injection, common rail engine test that measures engine power loss, which relates to fuel detergent additive efficiency. Lower power loss values indicate better detergent performance. The test engine is representative of new engines coming into the market.

[0110] Each composition uses the same base fuel and contains 71 ppm, on an actives basis, of the additive being evaluated. The results obtained are as follows:

Table 2 – DW-10 Engine Test Results

Fuel Sample	Additive Evaluated	Percent Power Change at EOT
4	None – Base Fuel alone	-5.1%
5	Inventive Example B	+2.1%
6	Inventive Example D	+1.1%
7	Comparative Example E	-3.4%
8	Comparative Example F	+2.0%

5

[0111] The results show that the Inventive Example B and D additives performs about as well as the quaternized polyisobutylene succinimide detergent of Example F and much better than the non-quaternized polyisobutylene succinimide detergent of Example E. All of the examples perform better than the base fuel alone, however the additives of Examples B, D and F perform significantly better than the base fuel.

10

[0112] As discussed herein, the comparable DW-10 engine performance delivered by Inventive Examples B, D and Comparative Example F is important when one then considers the superior viscosity and materials handling properties of Inventive Examples B and D, further demonstrated below.

15

Viscometric & Materials Handling Properties

[0113] Material handling properties, which may be evaluated by considering the kinematic viscosity of a material, significantly impact how easily a material may be used in commercial products and/or the amount of diluent that needs to be added to make the materials sufficiently handle-able, adding cost, complexity and waste to the overall process. Generally speaking, the lower the viscosity at 100°C the better the material handling properties. For a proper comparison, the kinematic viscosities of materials should be compared at an equal actives level, that is, with the same amount of diluent oil and similar materials present.

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[0114] To this end, Examples B, D and F were tested for viscosity at their original actives levels, about 85% actives for Example B and D, and about 75% actives for Example F. Examples B and D were also tested for viscosity at 75%

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actives, all on a weight basis, to allow for a better comparison to Example F. The reduced actives samples are prepared by mixing the example additive with an appropriate amount of 2-ethylhexanol. The viscosities of these blends were then determined using ASTM D445. The results obtained are presented below:

5 *Table 3 – Viscometric Data*

Example	KV100 (cSt) at about 85% actives (15% diluent)	KV100 (cSt) at about 75% actives (25% diluent)
B	79	23
D	47	39
F		100

[0115] The results show that Inventive Examples B and D have a significantly lower kinematic viscosity at 100°C compared to Comparative Example F, where the samples are considered at an actives level of 75%. These results indicate that the Inventive Samples have significantly better material handling properties and could be more easily utilized in higher concentrations without handling problems compared to the additives of Comparative Examples E and F.

Example G – Quaternized Polyester Amide Salt Detergent (inventive example)

[0116] A quaternized polyester amide salt detergent is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 3501 grams of the non-quaternized polyester amide of Example A, 80.4 grams of acetic acid, 24.5 grams of water, and 141.3 ml of propylene oxide, where the reaction is carried out at about 75°C and the propylene oxide is fed in to the reaction vessel over about 4 hours with moderate stirring. The reaction mixture is then held at temperature for about 3 hours. 3710.5 grams of product is cooled and collected, which TAN, FTIR and ESI-MS analysis confirms to be >90% by weight quaternized polyester amide salt detergent, with the remaining material being primarily non-quaternized polyester amide. The collected material has a TAN of 0 mg KOH/gram, a TBN of 27.76 mg KOH/gram, a kinematic viscosity at 100°C of 327.4 cSt (as measured by ASTM D445), an acetate peak by IR at 1575 cm⁻¹, and is 1.42% nitrogen.

Example H – Quaternized Polyester Amide Salt Detergent (inventive example)

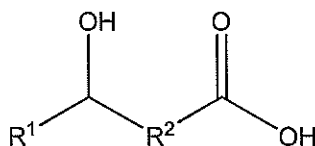
[0117] A quaternized polyester amide salt detergent is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system, 3401 grams of the non-quaternized polyester amide of Example C, 107.3 grams of acetic acid, 32.0 grams of water, and 1875.1 ml of propylene oxide, where the reaction is carried out at about 75°C and the propylene oxide is fed in to the reaction vessel over about 3.5 hours with moderate stirring. The reaction mixture is then held at temperature for about 3 hours. 3687.8 grams of product is cooled and collected, which TAN, FTIR and ESI-MS analysis confirms to be >90% by weight quaternized polyester amide salt detergent, with the remaining material being primarily non-quaternized polyester amide. The collected material has a TAN of 0 mg KOH/gram, a TBN of 26.4 mg KOH/gram, a kinematic viscosity at 100°C of 201.3 cSt (as measured by ASTM D445), an acetate peak by IR at 1574 cm⁻¹, and is 1.33% nitrogen.

[0118] 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." Except where otherwise indicated, all numerical quantities in the description specifying amounts or ratios of materials are on a weight basis. 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. As used herein, the expression "consisting essentially of" permits the

inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

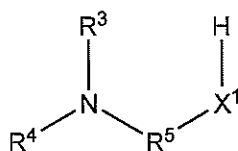
What is claimed is:

1. A composition comprising a quaternized polyester amide salt which
5 comprises the reaction product of:
 - a. a polyester amide containing a tertiary amino group; and
 - b. quaternizing agent selected from ethylene oxide, propylene oxide,
butylene oxide, styrene oxide, or a combination thereof used in combination
with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl
10 salicylate.
2. The composition of claim 1 wherein the polyester amide comprises the
reaction product of a fatty carboxylic acid containing at least one hydroxyl
group and a compound having a nitrogen atom capable of condensing with said
15 acid wherein said compound contains a tertiary amino group.
3. The composition of claim 2 wherein the fatty carboxylic acid is repre-
sented by the formula:



- 20 where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms; and

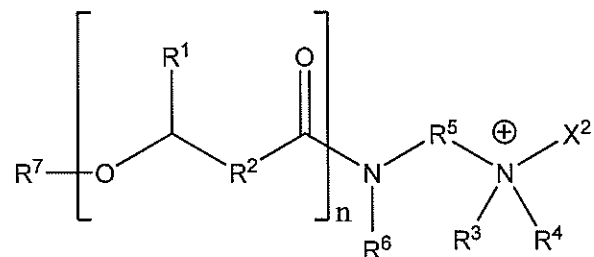
wherein the compound having a nitrogen atom capable of condensing with said acid and further having a tertiary amino group is represented by the
25 formula:



where R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene

group containing from 1 to 20 carbon atoms; and X^1 is NR^6 where R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms;

4. The composition of claim 1 wherein the quaternized polyester amide salt
5 comprises a cation represented by the following formula:



- where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; n is a number from 1 to 10; R^7 is hydrogen, a hydrocarbonyl group containing from 1 to 22 carbon atoms, or a hydrocarbyl group containing from 1 to 22 carbon atoms; and X^2 is a group
15 derived from the quaternizing agent.

5. The composition of claim 2 wherein the compound having a nitrogen atom capable of condensing with said acid and further having a tertiary amino group comprises N,N-diethylethylenediamine, N,N-dimethylethylenediamine,
20 N,N-dibutylethylenediamine, N,N-dimethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, or combinations thereof.

6. The composition of claim 2 wherein the fatty carboxylic acid containing at least one hydroxyl group comprises: 12-hydroxystearic acid; ricinoleic acid;
25 12-hydroxy dodecanoic acid; 5-hydroxy dodecanoic acid; 5-hydroxy decanoic acid; 4-hydroxy decanoic acid; 10-hydroxy undecanoic acid; or combinations thereof.

7. The composition of any one of claims 1 to 6, further comprising a metal deactivator, a composition other than those of claim 1, a dispersant, a viscosity modifier, a friction modifier, a dispersant viscosity modifier, an extreme pressure agent, an antiwear agent, an antioxidant, a corrosion inhibitor, a foam inhibitor, a demulsifier, a pour point depressant, a seal swelling agent, a wax control polymer, a scale inhibitor, a gas-hydrate inhibitor, or combinations thereof.
8. The composition of any one of claims 1 to 7, further comprising an overbased metal containing detergent, a zinc dialkyldithiophosphate, or combinations thereof.
9. The composition of any one of claims 1 to 8, further comprising a fuel which is liquid at room temperature.
10. The method of fueling an internal combustion engine comprising:
- A. supplying to said engine:
 - i. a fuel which is liquid at room temperature; and
 - ii. a composition comprising a quaternized polyester amide salt which comprises the reaction product of: (a) a polyester amide containing a tertiary amino group; and (b) quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate.
11. A process of making a quaternary ammonium polyester amide salt detergent comprising:
- I. reacting (a) a polyester amide containing a tertiary amino group; and (b) quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate;
- thereby obtaining the quaternized dispersant.

12. The process of claim 11 wherein the polyester amide containing a tertiary amino group is prepared by a process comprising:

- I. reacting (a)(i) a fatty carboxylic acid containing at least one hydroxyl group and (a)(ii) a compound having a nitrogen atom capable of condensing with said acid and further having a tertiary amino group;
5 thereby obtaining the polyester amide containing a tertiary amino group.