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# (54) QUATERNARY AMMONIUM SALTS IN HEATING OILS

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## (57) ABSTRACT

The invention relates to heating oils continuing quaternary ammonium salts, including succinimide, Mannich, polyalkylene substituted amine, quaternary ammonium salts. The invention also relates to the use of such salts in heating oil compositions and the use of such heating oil compositions in heating systems such as furnaces.

# QUATERNARY AMMONIUM SALTS IN HEATING OILS

## FIELD OF THE INVENTION

**[0001]** The invention relates to heating oils continuing quaternary ammonium salts, including succinimide, Mannich, polyalkylene substituted amine, quaternary ammonium salts. The invention also relates to the use of such salts in heating oil compositions and the use of such heating oil compositions in heating systems such as furnaces.

## BACKGROUND OF THE INVENTION

**[0002]** Home heating systems can use a variety of fuels, ranging from coal to natural gas. One commonly used fuel is heating oil. This fuel is easily delivered and can be stored in tanks on site near the equipment using the heating oil, for example a furnace.

**[0003]** Home heating applications typically use open flame burners, which are significantly different from combustion chambers utilized in other applications. Thus home heating applications present unique problems and challenges that are often different from the problems seen in other applications. Some problems are seen in both home heating applications and other application that use a different type of combustion chamber, however, due to the different in design and operation of home heating applications, solutions for problems do not generally carry over from one application to the other. In other words, home heating applications have different equipment and modes of operation than other applications that utilize combustion chambers, and home heating applications present unique problems and require unique solutions to address those problems.

**[0004]** In home heating applications, burning home heating oil over time can leave deposits on the nozzle tip where the heating oil composition is delivered to the burner. These deposits can disrupt the spray pattern, causing incomplete combustion and increased emissions. It is therefore desirable to prevent the soot from forming on the nozzle tip.

**[0005]** Additives based on the reaction product of polyisobutenyl succinic anhydride (PIBSA) and polyamines have been shown to reduce the level of soot on nozzle tips. One way of evaluating such additive performance is with the XUD-9 engine test. The XUD-9 test measures an additives ability to prevent the buildup of soot deposits on tips of injectors. It has been found that those additives that work comparatively better in the XUD-9 test also perform comparatively better in preventing nozzle deposit buildup in home heating applications.

**[0006]** However, there is demand for improved soot and deposit control in home heating applications and there is also demand for good performance provided at lower costs, which effectively means lower additive treat rate, in home heating applications. Thus there is a need for additives that provide improved soot control and/or deposit reduction in home heating applications.

## SUMMARY OF THE INVENTION

**[0007]** The present invention deals with a heating oil composition comprising: (A) a heating oil; and (B) a quaternary ammonium salt; where the quaternary ammonium salt comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen.

**[0008]** The invention provides for various embodiments of component (i), the compound comprising at least one tertiary amino group, including: (a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent wherein the condensation product has at least one tertiary amino group; (b) a polyalkene-substituted amine having at least one tertiary amino group; (c) a Mannich reaction product having at least one tertiary amino group, wherein the Mannich reaction product is derived from a hydrocarbyl-substituted phenol, an aldehyde, and an amine; or (d) any combination thereof.

**[0009]** The invention provides for various embodiments of component (ii), the quaternizing agent suitable for converting the tertiary amino group of compound, including: (a) dialkyl sulfates; (b) benzyl halides; (c) hydrocarbyl substituted carbonates; (d) hydrocarbyl epoxides optionally in combination with an acid; (e) esters of polycarboxylic acids; or (f) any combination thereof.

**[0010]** The invention further provides for a method of operating a heating device comprising the steps of: supplying to said heating device a heating oil composition comprising (A) a heating oil; and (B) a quaternary ammonium salt; wherein the quaternary ammonium salt comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. The quaternary ammonium salt may be any of the compounds described herein, made from any of the components described herein.

**[0011]** The invention further provides for the use of a quaternary ammonium salt as a soot modifier in a heating oil composition; wherein the quaternary ammonium salt comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. The quaternary ammonium salt may be any of the compounds described herein and can be made from any of the components described herein.

## DETAILED DESCRIPTION OF THE INVENTION

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

**[0013]** The invention provides a heating oil composition comprising: (A) a heating oil; and (B) a quaternary ammonium salt; wherein the quaternary ammonium salt detergent comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. The various components are described in greater detail below.

### The Heating Oil

**[0014]** The heating oils, which in some embodiments may be referred to as home heating oils (HHO) and/or furnace fuel oils (FFO), suitable for use in the present invention are not overly limited and may include all heating oil suitable for use in home heating applications. In general heating oils are relatively low viscosity, flammable liquid petroleum products used as fuel for furnaces or boilers in homes and other buildings.

**[0015]** Heating oil is commonly delivered by tank truck to customers in residential, commercial and municipal buildings. The heating oil is typically stored in underground storage tanks (UST) or above-ground storage tanks (AST). AST are generally located in garages or outside the buildings, but may also be located in the basements of the buildings. Heating oil is generally not used as an industrial fuel or for power generation, but rather is more common for smaller scale applications such as home heating.

**[0016]** In some embodiments the heating oil of the invention consists of a mixture of petroleum-derived hydrocarbons containing from 14 to 20 carbon atoms with a condensation/distillation point between 250 and 350° C. Heating oil generally distills at a lower temperature than the heavy hydrocarbons (those that contain more than 20 carbon atoms) such as petroleum jelly, bitumen, candle wax, and lubricating oils, which typically distills between 340 and 400° C., while it generally distills at a higher temperature than kerosene, which distills between 160 and 250° C.

**[0017]** The fuel may also be a blend of petroleum-derived hydrocarbons and fuels derived from a bio source. In some embodiments the fuel may contain a portion derived from a bio source such as biodiesel. The biodiesel portion of the fuel may be up to 20%. Suitable biodiesel is typically in the form of, but not limited to, methyl esters of the fatty acids from soybean, rapeseed, or palm oils.

**[0018]** The heating oil compositions of the present invention may include one or more additives other than the quaternary ammonium salt described below. Such 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. 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 heating oil compositions: antioxidants, corrosion inhibitors, detergent and/or dispersant additives other than those described above, cold flow improvers, foam inhibitors, demulsifiers, lubricity agents, metal deactivators, biocides, antistatic agents, deicers, fluidizers, combustion improvers, wax control polymers, scale inhibitors, or any combination thereof.

**[0019]** 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 benzotriazole. Suitable foam inhibitors and/or antifoams include for example organic silicones such as polydimethylsiloxane, polyethylsiloxane, polydiethylsiloxane, polyacrylates and polymethacrylates, trimethyl-trifluoro-propylmethylsiloxane and the like. Suitable fluidizers include for example mineral oils and/or poly(alpha-olefins) and/or polyethers. Combustion improvers include for example iron, cerium or platinum compounds.

**[0020]** 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 linear or branched, but in some embodiments are derived from branched alcohols resulting in friction modifiers that themselves have significant amounts of branched hydrocarbyl groups present within it structure. Examples of suitable branched alcohols used to prepare such friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, and mixtures thereof.

**[0021]** 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. Pat. Nos. 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. Pat. No. 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. Pat. No. 3,634,515. 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.

**[0022]** Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, 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. Pat. No. 4,654,403.

**[0023]** The compositions of the invention may include a detergent additive, different from the quaternized salt additive of the invention.

**[0024]** 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 hydrocarbyl group or a group bridging two aromatic rings. The latter antioxidants are described in greater detail in U.S. Pat. No. 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.

**[0025]** 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) such as 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.

**[0026]** Multifunctional viscosity improvers, which also have dispersant and/or antioxidancy 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.

**[0027]** Any of the additional performance additives described above may be added to the compositions of the present invention. 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.

**[0028]** In some embodiments the heating oil compositions of the invention includes one or more of the following additional additives: an alcohol, a phenolic antioxidant, an alkaryl amine antioxidant, a triazole metal deactivator, a polyisobutylene succinic acid, a demulsifier, a petroleum naphtha solvent, and an additional antioxidant booster.

## The Quaternary Ammonium Salt

**[0029]** The quaternary ammonium salts of the present invention include the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. Various embodiments of suitable quaternary ammonium salts are described herein and the invention contemplates the use of any one of them or combination thereof.

**[0030]** The compositions of the present invention comprise a quaternary ammonium salt. The quaternary ammonium salt may be the reaction product of: (i) at least one compound which may include: (a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent where the condensation product has at least one tertiary amino group; (b) a polyalkene-substituted amine having at least one tertiary amino group; and (c) a Mannich reaction product having at least one tertiary amino group, where the Mannich reaction product is derived from a hydrocarbyl-substituted phenol, an aldehyde, and an amine; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. The quaternizing agent may include dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, and hydrocarbyl epoxides, any of which may be used in combination with an acid.

**[0031]** The compounds of component (i)(a), (i)(b) and (i)(c), described in greater detail below, contain at least one tertiary amino group and include compounds that may be alkylated to contain at least one tertiary amino group after an alkylation step. In some embodiments the quaternary ammonium salt may be the reaction product of a polyalkene chloride, for example polyisobutylene chloride and a compound with a tertiary amine. In such embodiments the polyisobutylene chloride is the quaternizing agent and the compound with a tertiary amine is component (i). Suitable example of component (i) for such embodiments includes tertiary amines such as trimethylamine.

**[0032]** Examples of quaternary ammonium salt and methods for preparing the same are described in U.S. Pat. Nos. 4,253,980; 3,778,371; 4,171,959; 4,326,973; 4,338,206; and 5,254,138.

**[0033]** The quaternary ammonium salts may be prepared in the presence of a solvent, which may or may not be removed once the reaction is complete. Suitable solvents include, but are not limited to, diluent oil, petroleum naphtha, and certain alcohols. In one embodiment, these alcohols contain at least 2 carbon atoms, and in other embodiments at least 4, at least 6 or at least 8 carbon atoms. In another embodiment, the solvent of the present invention contains 2 to 20 carbon atoms, 4 to 16 carbon atoms, 6 to 12 carbon atoms, 8 to 10 carbon atoms, or just 8 carbon atoms. These alcohols often have a 2-($C_{1-4}$ alkyl) substituent, namely, methyl, ethyl, or any isomer of propyl or butyl. 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-methylheptanol, or combinations thereof. In one embodiment the solvent of the present invention includes 2-ethylhexanol.

## Succinimide Quaternary Ammonium Salts

**[0034]** In one embodiment the quaternary salt detergent comprises the reaction product of (i)(a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent where the condensation product has at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen.

**[0035]** Hydrocarbyl substituted acylating agents useful in the present invention include the reaction product of a long chain hydrocarbon, generally a polyolefin, with a monounsaturated carboxylic acid or derivative thereof.

**[0036]** Suitable monounsaturated carboxylic acids or derivatives thereof include: (i) α,β-monounsaturated $C_4$ to $C_{10}$ dicarboxylic acids, 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 acids, such as acrylic acid and methacrylic acid; or (iv) derivatives of (iii), such as $C_1$ to $C_5$ alcohol derived esters of (iii).

**[0037]** Suitable long chain hydrocarbons for use in preparing the hydrocarbyl substituted acylating agents include any compound containing an olefinic bond represented by the general Formula I, shown here:

$$(R^1)(R^2)C{=}C(R^3)(CH(R^4)(R^5)) \qquad (I)$$

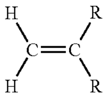
wherein each of $R^1$, $R^2$, $R^3$, $R^4$ and $R^5$ is, independently, hydrogen or a hydrocarbon based group. In some embodiments at least one of $R^3$, $R^4$ or $R^5$ is a hydrocarbon based group containing at least 20 carbon atoms.

**[0038]** These long chain hydrocarbons, which may also be described as polyolefins or olefin polymers, are reacted with the monounsaturated carboxylic acids and derivatives described above to form the hydrocarbyl substituted acylating agents used to prepare the nitrogen-containing detergent of the present invention. Suitable olefin polymers include polymers comprising a major molar amount of $C_2$ to $C_{20}$, or $C_2$ to $C_5$ mono-olefins. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, or styrene. The polymers may be homo-polymers, such as polyisobutylene, as well as copolymers of two or more of such olefins. Suitable copolymers include copolymers of ethylene and propylene, butylene and isobutylene, and propylene and isobutylene. Other suitable copolymers include those in which a minor molar amount of the copolymer monomers, e.g. 1 to 10 mole %, is a $C_4$ to $C_{18}$ di-olefin. Such copolymers include: a copolymer of isobutylene and butadiene; and a copolymer of ethylene, propylene and 1,4-hexadiene.

**[0039]** In one embodiment, at least one of the —R groups of Formula (I) shown above is derived from polybutene, that is, polymers of $C_4$ olefins, including 1-butene, 2-butene and isobutylene. $C_4$ polymers include polyisobutylene. In another embodiment, at least one of the —R groups of Formula I is derived from ethylene-alpha olefin polymers, including ethylene-propylene-diene polymers. Examples of documents that described ethylene-alpha olefin copolymers and ethylene-lower olefin-diene ter-polymers include U.S. Pat. Nos. 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; and 5,324,800.

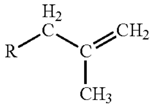
**[0040]** In another embodiment, the olefinic bonds of Formula (I) are predominantly vinylidene groups, represented by the following formula:

(II)



wherein each R is a hydrocarbyl group; which in some embodiments may be:

(III)



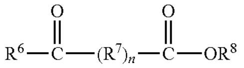
wherein R is a hydrocarbyl group.

**[0041]** In one embodiment, the vinylidene content of Formula (I) may comprise at least 30 mole % vinylidene groups, at least 50 mole % vinylidene groups, or at least 70 mole % vinylidene groups. Such materials and methods of preparation 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 United States publications: 2004/0176552A1; 2005/0137363; and 2006/0079652A1. Such products are commercially available from BASF, under the trade name GLISSOPAL™ and from Texas PetroChemical LP, under the trade name TPC 1105™ and TPC 595™.

**[0042]** Methods of making hydrocarbyl substituted acylating agents from the reaction of monounsaturated carboxylic acid reactants and compounds of Formula (I) are well known in the art and disclosed in: U.S. Pat. Nos. 3,361,673; 3,401,118; 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; and 6,165,235.

**[0043]** In another embodiment, the hydrocarbyl substituted acylating agent can be made from the reaction of a compound represented by Formula (I) with at least one carboxylic reactant represented by the following formulas:

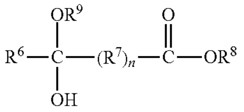
(IV)



$$R^6-\overset{\displaystyle O}{\overset{\|}{C}}-(R^7)_n-\overset{\displaystyle O}{\overset{\|}{C}}-OR^8$$

and

(V)



$$R^6-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle OR^9}{\overset{|}{C}}}}-(R^7)_n-\overset{\displaystyle O}{\overset{\|}{C}}-OR^8$$

wherein each of $R^6$, $R^8$ and $R^9$ is independently H or a hydrocarbyl group, $R^7$ is a divalent hydrocarbylene group, and n is 0 or 1. Such compounds and the processes for making them 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.

**[0044]** In yet another embodiment, the hydrocarbyl substituted acylating agent may be made from the reaction of any compound represented by Formula (I) with any compound represented by Formula (IV) or Formula (V), where the reaction is 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, as well as higher aldehydes. Other aldehydes, such as dialdehydes, especially glyoxal, are useful, although monoaldehydes are generally preferred. In one embodiment, the aldehyde is formaldehyde, which may be supplied in the aqueous solution often referred to as formalin, but which is more often used in the polymeric form referred to as paraformaldehyde. Paraformaldehyde is considered a reactive equivalent of and/or source of formaldehyde. Other reactive equivalents include hydrates or cyclic trimers. Suitable ketones include acetone, butanone, methyl ethyl ketone, as well as other ketones. In some embodiments, one of the two hydrocarbyl groups of the ketone is a methyl group. Mixtures of two or more aldehydes and/or ketones are also useful. Such hydrocarbyl substituted acylating agents and the processes for making them are disclosed in U.S. Pat. Nos. 5,840,920; 6,147,036; and 6,207,839.

**[0045]** In another embodiment, the hydrocarbyl substituted acylating agent may include methylene bis-phenol alkanoic acid compounds. Such compounds may be the condensation product of (i) an aromatic compound of the formula:

$$R_m\text{—Ar—}Z_c \qquad \text{(VI)}$$

and (ii) at least on carboxylic reactant such as the compounds of formula (IV) and (V) described above, wherein, in Formula (VI): each R is independently a hydrocarbyl group; 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 group available for substitution; Ar is an aromatic group or moiety containing from 5 to 30 carbon atoms and from 0 to 3 optional substituents such as amino, hydroxy- or alkyl-polyoxyalkyl, nitro, aminoalkyl, and carboxy groups, or combinations of two or more of said optional substituents; Z is independently —OH, —O, a lower alkoxy group, or $\text{—}(OR^{10})_bOR^{11}$ wherein each $R^{10}$ is independently a divalent hydrocarbyl group, b is a number from 1 to 30, and $R^{11}$ is —H or a hydrocarbyl group; and c is a number ranging from 1 to 3.

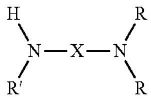
**[0046]** In one embodiment, at least one hydrocarbyl group on the aromatic moiety is derived from polybutene. In one embodiment, the source of the hydrocarbyl groups described above are polybutenes obtained by polymerization of isobutylene in the presence of a Lewis acid catalyst such as aluminum trichloride or boron trifluoride. Such compounds and the processes for making them 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.

**[0047]** 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. Such compounds and the processes for making them are disclosed in U.S. Pat. No. 5,620,949. Still other methods of making suitable hydrocarbyl substituted acylating agents can be found in U.S. Pat. Nos. 5,912,213; 5,851,966; and 5,885,944.

**[0048]** The succinimide quaternary ammonium salt detergents are derived by reacting the hydrocarbyl substituted acylating agent described above with a compound having an oxygen or nitrogen atom capable of condensing with the acylating agent. In one embodiment, suitable compounds contain at least one tertiary amino group or may be alkylated until they contain a tertiary amino group, so long as the hydrocarbyl substituted acylating agent has at least one tertiary amino group when it is reacted with the quaternizing agent.

**[0049]** In one embodiment, this compound may be represented by one of the following formulas:

(VII)

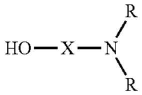


$$\text{H(R}')\text{N—X—NR}_2$$

and

-continued

(VIII)



$$\text{HO—X—NR}_2$$

Wherein, for both Formulas (VII) and (VIII), each X is independently a alkylene group containing 1 to 4 carbon atoms; and each R is independently a hydrocarbyl group and R' is a hydrogen or a hydrocarbyl group.

**[0050]** Suitable compounds include but are not limited to: 1-aminopiperidine, 1-(2-aminoethyl)piperidine, 1-(3-aminopropyl)-2-pipecoline, 1-methyl-(4-methylamino)piperidine, 1-amino-2,6-dimethylpiperidine, 4-(1-pyrrolidinyl)piperidine, 1-(2-aminoethyl)pyrrolidine, 2-(2-aminoethyl)-1-methylpyrrolidine, N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, 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 some embodiments the amine used is 3-dimethylaminopropylamine, 3-diethylaminopropylamine, 1-(2-aminoethyl)pyrrolidine, N,N-dimethylethylenediamine, or combinations thereof.

**[0051]** Suitable compounds further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-amino ethyl)piperidine, 3,3-diamino-N-methyldipropylamine, 3,3'-aminobis(N,N-dimethylpropylamine) These have been mentioned in previous list.

**[0052]** Still further nitrogen or oxygen containing compounds capable of condensing with the acylating agent which also have a tertiary amino group include: alkanolamines, including but not limited to triethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, and N,N-diethylaminobutanol, N,N,N-tris(hydroxyethyl)amine.

**[0053]** The succinimide quaternary ammonium salt detergents of the present invention are formed by combining the reaction product described above (the reaction product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and further having at least one tertiary amino group) with a quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen. Suitable quaternizing agents are discussed in greater detail below. In some embodiments these preparations may be carried out neat or in the presence of a solvent, as described above. By way of non-limiting example, preparations of succinimide quaternary ammonium salts are provided below.

**[0054]** In some embodiments the compositions of the invention are substantially free of, or even completely free of, the succinimide quaternary ammonium salts described above.

## Polyalkene-Substituted Amine Quaternary Ammonium Salts

**[0055]** In one embodiment the quaternary ammonium salt is the reaction product of: (i)(b) a polyalkene-substituted amine having at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen.

**[0056]** Suitable polyalkene-substituted amines may be derived from an olefin polymer and an amine, such as ammonia, monoamines, polyamines or mixtures thereof. They may be prepared by a variety of methods. Suitable polyalkene-substituted amines or the amines from which they are derived either contain a tertiary amino group or may be alkylated until they contain a tertiary amino group, so long as the polyalkene-substituted amine has at least one tertiary amino group when it is reacted with the quaternizing agent.

**[0057]** One method of preparation of a polyalkene-substituted amine involves reacting a halogenated olefin polymer with an amine, as disclosed in U.S. Pat. Nos. 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,755,433; and 3,822,289. Another method of preparation of a polyalkene-substituted amine involves reaction of a hydro-formylated olefin with a polyamine and hydrogenating the reaction product, as disclosed in U.S. Pat. Nos. 5,567,845 and 5,496,383. Another method for preparing a polyalkene-substituted amine involves converting a polyalkene, by means of a conventional epoxidation reagent, with or without a catalyst, into the corresponding epoxide and converting the epoxide into the polyalkene substituted amine by reaction with ammonia or an amine under the conditions of reductive amination, as disclosed in U.S. Pat. No. 5,350,429. Another method for preparing a polyalkene-substituted amine involves hydrogenation of a β-aminonitrile, made by reacting an amine with a nitrile, as disclosed in U.S. Pat. No. 5,492,641. Yet another method for preparing a polyalkene-substituted amine involves hydroformylating polybutene or polyisobutylene, with a catalyst, such as rhodium or cobalt, in the presence of CO, $H_2$ and $NH_3$ at elevated pressures and temperatures, as disclosed in U.S. Pat. Nos. 4,832,702; 5,496,383 and 5,567,845. The above methods for the preparation of polyalkene substituted amine are for illustrative purposes only and are not meant to be an exhaustive list. The polyalkene-substituted amines of the present invention are not limited in scope to the methods of their preparation disclosed hereinabove.

**[0058]** The polyalkene-substituted amine may be derived from olefin polymers. Suitable olefin polymers for preparing the polyalkene-substituted amines of the invention are the same as those described above.

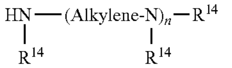
**[0059]** The polyalkene-substituted amine may be derived from ammonia, monoamines, polyamines, or mixtures thereof, including mixtures of different monoamines, mixtures of different polyamines, and mixtures of monoamines and polyamines (which include diamines). Suitable amines include aliphatic, aromatic, heterocyclic and carbocyclic amines.

**[0060]** In one embodiment, the amines may be characterized by the formula:

$$R^{12}R^{13}NH \tag{IX}$$

wherein $R^{12}$ and $R^{13}$ are each independently hydrogen, hydrocarbon, amino-substituted hydrocarbon, hydroxy-substituted hydrocarbon, alkoxy-substituted hydrocarbon, or acylimidoyl groups provided that no more than one of $R^{12}$ and $R^{13}$ is hydrogen. The amine may be characterized by the presence of at least of at least one primary ($H_2N$—) or secondary amino (H—N<) group. These amines, or the polyalkene-substituted amines they are used to prepare may be alkylated as needed to ensure they contain at least one tertiary amino group. Examples of suitable monoamines include ethylamine, dimethylamine, diethylamine, n-butylamine, dibutylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleylamine, N-methyl-octylamine, dodecylamine, diethanolamine, morpholine, and octadecylamine.

**[0061]** The polyamines from which the detergent is derived include principally alkylene amines conforming, for the most part, to the formula:


(X)

$$\underset{\displaystyle R^{14}}{HN}—(\text{Alkylene-}\underset{\displaystyle R^{14}}{N})_n—R^{14} \tag{X}$$

wherein n is an integer typically less than 10, each $R^{14}$ is independently hydrogen or a hydrocarbyl group typically having up to 30 carbon atoms, and the alkylene group is typically an alkylene group having less than 8 carbon atoms. The alkylene amines include principally, ethylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines. They are exemplified specifically by: ethylenediamine, diethylenetriamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(-trimethylene)triamine, aminopropylmorpholine and dimethylaminopropylamine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful. Tetraethylene pentamine is particularly useful.

**[0062]** The ethylene amines, also referred to as polyethylene polyamines, are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk and Othmer, Vol. 5, pp. 898-905, Interscience Publishers, New York (1950).

**[0063]** Any of the above polyalkene-substituted amines, or the amines from which they are derived, which are secondary or primary amines, may be alkylated to tertiary amines using alkylating agents before or while they are reacted with the quaternizing agents to form the quaternary ammonium salt additives of the present invention. Suitable alkylating agents include the quaternizing agents discussed below.

**[0064]** The polyalkene-substituted amine quaternary ammonium salts of the present invention are formed by combining the reaction product described above (the polyalkene-substituted amine, having at least one tertiary amino group) with a quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen. Suitable quaternizing agents are discussed in greater detail below. By way of non-limiting example, a preparation of a polyalkene-substituted amine quaternary ammonium salt is provided below.

**[0065]** In some embodiments the compositions of the invention are substantially free of, or even completely free of, the polyalkene-substituted amine quaternary ammonium salts described above.

Mannich Quaternary Ammonium Salts

**[0066]** In one embodiment the quaternary ammonium salt is the reaction product of: (i)(c) a Mannich reaction product; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. Suitable Mannich reaction products have at least one tertiary amino group and are prepared from the reaction of a hydrocarbyl-substituted phenol, an aldehyde, and an amine.

**[0067]** The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 10 to 400 carbon atoms, in another instance 30 to 180 carbon atoms, and in a further instance 10 or 40 to 110 carbon atoms. This hydrocarbyl substituent can be derived from an olefin or a polyolefin. Useful olefins include alpha-olefins, such as 1-decene, which are commercially available. Suitable polyolefins include those described in the sections above. The hydrocarbyl-substituted phenol can be prepared by alkylating phenol with one of these suitable olefins or polyolefins, such as a polyisobutylene or polypropylene, using well-known alkylation methods.

**[0068]** The aldehyde used to form the Mannich detergent can have 1 to 10 carbon atoms, and is generally formaldehyde or a reactive equivalent thereof, such as formalin or paraformaldehyde.

**[0069]** The amine used to form the Mannich detergent can be a monoamine or a polyamine. Amines suitable for preparing the Mannich reaction product of the invention are the same as those are described in the sections above.

**[0070]** In one embodiment, the Mannich detergent is prepared by reacting a hydrocarbyl-substituted phenol, an aldehyde, and an amine, as described in U.S. Pat. No. 5,697,988. In one embodiment, the Mannich reaction product is prepared from: an alkylphenol derived from a polyisobutylene; formaldehyde; and a primary monoamine, secondary monoamine, or alkylenediamine. In some of such embodiments the amine is ethylenediamine or dimethylamine. Other methods of preparing suitable Mannich reaction products can be found in U.S. Pat. Nos. 5,876,468 and 5,876,468.

**[0071]** As discussed above, it may be necessary, with some of the amines, to further react the Mannich reaction product with an epoxide or carbonate, or other alkylating agent, in order to obtain the tertiary amino group.

**[0072]** The Mannich quaternary ammonium salts of the present invention are formed by combining the reaction product described above (the Mannich reaction product with at least one tertiary amino group) with a quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen. Suitable quaternizing agents are discussed below.

**[0073]** In some embodiments the compositions of the invention are substantially free of, or even completely free of, the Mannich quaternary ammonium salts described above.

Amide and/or Ester Quaternary Ammonium Salts

**[0074]** In some embodiments the quaternary ammonium salts used in the invention are quaternary amide and/or ester detergents which may be described as the reaction product of: (i) a non-quaternized amide and/or ester detergent having a tertiary amine functionality; and (ii) a quaternizing agent. In some embodiments the non-quaternized detergent is the condensation product of (a) a hydrocarbyl-substituted acylating agent and (b) a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and further having at least one tertiary amino group.

**[0075]** The non-quaternized amide and/or ester detergents suitable for use in the present invention include the condensation product of (i) a hydrocarbyl-substituted acylating agent and (ii) a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and further having at least one tertiary amino group, where the resulting detergent has at least one tertiary amino group and also contains an amide group and/or an ester group. Typically, the compound having an oxygen or nitrogen atom capable of condensing with said acylating agent determined whether the resulting detergent contains an amide group or an ester group. In some embodiments, the non-quaternized detergent, and so the resulting quaternized detergent is free of any imide groups. In some embodiments, the non-quaternized detergent, and so the resulting quaternized detergent is free of any ester groups. In these embodiments the detergent contains at least one, or just one, amide group.

**[0076]** The hydrocarbyl substituted acylating agent can be any of the materials described in section above provided that the material contains an amide group and/or an ester group.

**[0077]** The non-quaternized amide and/or ester detergent used to prepare the additives of the present invention are themselves formed when the acylating agents described above are reacted with a compound having an oxygen or nitrogen atom capable of condensing with the acylating agent which further has at least one tertiary amino group. Any of these compounds described above may be used here as well.

**[0078]** The quaternary amide and/or ester detergents are prepared by reacting (a) the non-quaternized amide and/or ester detergent having a tertiary amine functionality with (b) the quaternizing agent; thereby obtaining the quaternized detergent. The processes of the present in invention may also be described as a process for preparing a quaternized amide and/or ester detergent comprising the steps of: (1) mixing (a) a non-quaternized amide and/or ester detergent having an amine functionality, (b) a quaternizing agent and optionally with (c) a protic solvent, which in some embodiments is free of methanol; (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 amide and/or ester 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 where the hydrocarbyl acylating agent is derived from a monocarboxylic acid, the reaction temperature may be 70° C. to 130° C. In other embodiments where the hydrocarbyl acylating agent is derived from a dicarboxylic acid, the reaction temperature may be 50° C. to 80° C. or 50° C. to 70° C. 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.

**[0079]** As described above, in some embodiments the non-quaternized amide and/or ester detergent is the condensation product of hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and further having at least one tertiary amino group. Suitable quaternizing agents and compounds having an oxygen or nitrogen atom are also described above.

**[0080]** The additives of the present invention may be derived in the presence of a protic solvent. In some embodiments the process used to prepare these additives is substantially free of to free of methanol. Substantially free of methanol can mean less than 0.5, 0.1 or 0.05 percent by weight methanol in the reaction mixture, and may also mean completely free of methanol.

**[0081]** 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 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 $C_1$-$C_6$ 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 diglycol ether, methoxytriglycol, ethoxytriglycol, butoxytriglycol, methoxytetraglycol, butoxytetraglycol.

**[0083]** Suitable solvents for use in the invention also include certain alcohols. In one embodiment, these alcohols contain at least 2 carbon atoms, and in other embodiments at least 4, at least 6 or at least 8 carbon atoms. In another embodiment, the solvent of the present invention contains 2 to 20 carbon atoms, 4 to 16 carbon atoms, 6 to 12 carbon atoms, 8 to 10 carbon atoms, or just 8 carbon atoms. These alcohols normally have a 2-($C_{1-4}$ alkyl) substituent, namely, methyl, ethyl, or any isomer of propyl or butyl. 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 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 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.

**[0087]** The solvent may be present such that the weight ratio of the amount of detergent having an amine functionality to the amount of polar solvent is in one set of embodiments from 20:1 to 1:20; or from 10:1 to 1:10. In additional embodiments, the detergent to solvent weight ratio can be from 1:10 to 1:15; from 15:1 to 10:1; or from 5:1 to 1:1.

**[0088]** In some embodiments the compositions of the invention are substantially free of, or even completely free of, the quaternary amide and/or ester detergents described above.

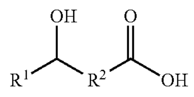
## Polyester Quaternary Ammonium Salts

**[0089]** In some embodiments the quaternary ammonium salt is a polyester quaternary salt, which may include quaternized polyester amine, amide, and ester salts. Such 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 quaternary agents may be any of the agents described herein.

**[0090]** 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.

**[0091]** 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 further having a tertiary amino group. Suitable fatty carboxylic acids to use in the preparation of the polyesters described above may be represented by the formula:

(XI)

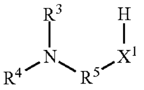


where $R^1$ is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and $R^2$ is a hydrocarbylene group containing from 1 to 20 carbon atoms. In some embodiments $R^1$ contains from 1 to 12, 2 to 10, 4 to 8 or even 6 carbon atoms, and $R^2$ contains from 2 to 16, 6 to 14, 8 to 12, or even 10 carbon atoms.

**[0092]** 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.

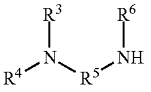
**[0093]** In some embodiments the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group is represented by the formula:

(XII)



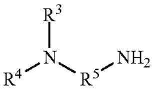
where $R^3$ is a hydrocarbyl group containing from 1 to 10 carbon atoms; $R^4$ is a hydrocarbyl group containing from 1 to 10 carbon atoms; $R^5$ is a hydrocarbylene group containing from 1 to 20 carbon atoms; and $X^1$ is O or $NR^6$ where $R^6$ is a hydrogen or a hydrocarbyl group containing from 1 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 (XII) becomes:

(XII-a)



or

(XII-b)



where the various definitions provided above still apply.

**[0094]** 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 any of the materials described in the sections above.

**[0095]** The nitrogen or oxygen containing compounds may further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine.

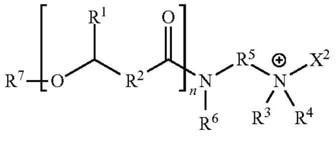
**[0096]** In one embodiment the nitrogen or oxygen containing compound is triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamino) ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanolamine, N-butyldiethanolamine, N,N-diethylamino ethanol, N,N-dimethylaminoethanol, 2-dimethylamino-2-methyl-1-propanol, or combinations thereof.

**[0097]** 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.

**[0098]** 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 amino alcohol is reacted with a monomer and then the resulting material is polymerized with additional monomer, giving the polyester amide which may then be quaternized.

**[0099]** In some embodiments the quaternized polyester salt includes a cation represented by the following formula:

(XIII)



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.

**[0100]** 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.

**[0101]** 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.

**[0102]** The number average molecular weight (Mn) of the quaternized polyester salts of the invention may be from 500 to 3000, or from 700 to 2500.

**[0103]** 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.

**[0104]** 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.

**[0105]** 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.

**[0106]** Specific examples of such hydroxycarboxylic acids include ricinoleic acid, a mixture of 9- and 10-hydroxystearic acids (obtained by sulphation of oleic acid and then hydrolysis), and 12-hydroxystearic acid, and the commercially available hydrogenated castor oil fatty acid which contains in addition to 12-hydroxystearic acid minor amounts of stearic acid and palmitic acid.

**[0107]** 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.

**[0108]** 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.

**[0109]** 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. In some embodiments these excluded agents are the reaction product of a long chain hydrocarbon, generally a polyolefin reacted with a monounsaturated carboxylic acid reactant, such as, (i) $\alpha,\beta$-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) $\alpha,\beta$-monounsaturated $C_3$ to $C_{10}$ monocarboxylic acid such as acrylic acid and methacrylic acid; or (iv) 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 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.

**[0110]** 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 embodiment is on polyester, or hyperdispersant, quaternary salt detergent additives.

**[0111]** In some embodiments the compositions of the invention are substantially free of, or even completely free of, the polyester quaternary salts described above.

## The Quaternizing Agent

**[0112]** Suitable quaternizing agents for preparing any of the quaternary ammonium salt detergents described above include dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl epoxides used in combination with an acid, esters of polycarboxylic acids, or mixtures thereof.

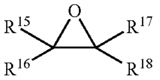
**[0113]** In one embodiment the quaternizing agent includes: halides such as chloride, iodide or bromide; hydroxides; sulphonates; alkyl sulphates such as dimethyl sulphate; sultones; phosphates; $C_{1-12}$ alkylphosphates; di-$C_{1-12}$ alkylphosphates; borates; $C_{1-12}$ alkylborates; nitrites; nitrates; carbonates; bicarbonates; alkanoates; O,O-di-$C_{1-12}$ alkyldithiophosphates; or mixtures thereof.

**[0114]** In one embodiment the quaternizing agent may be: a dialkyl sulphate such as dimethyl sulphate; N-oxides; sultones such as propane or butane sultone; alkyl, acyl or aralkyl halides such as methyl and ethyl chloride, bromide or iodide or benzyl chloride; hydrocarbyl (or alkyl) substituted carbonates; or combinations thereof. If the aralkyl halide is benzyl chloride, the aromatic ring is optionally further substituted with alkyl or alkenyl groups.

**[0115]** 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.

**[0116]** In another embodiment the quaternizing agent can be a hydrocarbyl epoxides, as represented by the following formula:

(XIV)



wherein $R^{15}$, $R^{16}$, $R^{17}$ and $R^{18}$ can be independently H or a $C_{1-50}$ hydrocarbyl group. Examples of suitable hydrocarbyl epoxides include: styrene oxide, ethylene oxide, propylene oxide, butylene oxide, stilbene oxide, $C_{2-50}$ epoxides, or combinations thereof.

**[0117]** 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:

$$R^{19}—C(=O)—O—R^{20} \qquad (XV)$$

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

**[0118]** 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 a-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.

**[0119]** 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.

**[0120]** 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.

**[0121]** 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 example include diesters of oxalic acid, diesters of phthalic acid, diesters of maleic acid, diesters of malonic acid or diesters or triesters of citric acid.

**[0122]** 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, methyl 2-nitrobenzoate and methyl salicylate.

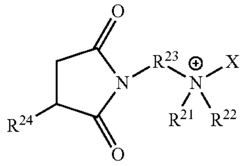
**[0123]** Any of the quaternizing agents described above, including the hydrocarbyl epoxides, may be used in combination with an acid. Suitable acids include carboxylic acids, such as acetic acid, propionic acid, 2-ethylhexanoic acid, and the like.

**[0124]** In some embodiments the quaternary ammonium salt includes the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, where component (i), the compound comprising at least one tertiary amino group, comprises: (a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent wherein the condensation product has at least one tertiary amino group.

**[0125]** In some embodiments the hydrocarbyl-substituted acylating agent may be polyisobutylene succinic anhydride and the compound having an oxygen or nitrogen atom capable of condensing with said acylating agent may be dimethylaminopropylamine, N-methyl-1,3-diaminopropane, N,N-dimethylaminopropylamine, N,N-diethyl-aminopropylamine, N,N-dimethylaminoethylamine, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetraamine, tetraethylenepentaamine, pentaethylenehexaamine, hexamethylenetetramine, and bis(hexamethylene)triamine.

**[0126]** In some embodiments the quaternary ammonium salt comprises an cation represented by the following formula:

(XVI)



wherein: $R^{21}$ is a hydrocarbyl group containing from 1 to 10 carbon atoms; $R^{22}$ is a hydrocarbyl group 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 50 to 150 carbon atoms; and X is a group derived from the quaternizing agent.

**[0127]** In some embodiments the quaternary ammonium salt includes the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, where component (i), the compound comprising at least one tertiary amino group, comprises: (b) a polyalkene-substituted amine having at least one tertiary amino group.

**[0128]** In some embodiments the polyalkene substituent of the polyalkene-substituted amine is derived from polyisobutylene and the polyalkene-substituted amine has a number average molecular weight of about 500 to about 3000.

**[0129]** In some embodiments the quaternary ammonium salt includes the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, where component (i), the compound comprising at least one tertiary amino group, comprises: (c) a Mannich reaction product having at least one tertiary amino group, wherein the Mannich reaction product is derived from a hydrocarbyl-substituted phenol, an aldehyde, and an amine.

**[0130]** In some embodiments component (i), the compound comprising at least one tertiary amino group, comprises a Mannich reaction product having a tertiary amino group, said Mannich reaction product being prepared from the reaction of a hydrocarbyl-substituted phenol, an aldehyde, and an amine; and wherein the hydrocarbyl substituent of the hydrocarbyl-substituted phenol of component (a) is derived from a polyolefin having a number average molecular weight of 400 to 3,000; wherein the aldehyde of component (a) is a formaldehyde or a reactive equivalent thereof; and wherein the amine of component (a) is selected from the group consisting of dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine, dibutylamine, and mixtures thereof.

**[0131]** In any of these embodiments described above, any of one or combination of quaternizing agents described above may be used.

## INDUSTRIAL APPLICATION

**[0132]** As noted above, home heating applications use specially designed burners, sometimes referred to as open air burners. Such burners are highly designed to increase burner efficiency in forced air furnaces and other similar home heating applications. These burners are very different from those seen on other application, especially the equipment designed for use in internal combustion engines, and present special problems and challenges unique to home heating applications.

**[0133]** In a forced-air furnace a pump may be used to drawn the heating oil from a storage tank and pressurize it to 1,034 kPa, forcing it through a nozzle to form an atomized spray. A pair of metal electrodes is typically used to ignite the heating oil, with the electrodes positioned near the heating oil spray nozzle such that high voltage formed across the electrode gap produces a spark approximately 6 mm long. With the airflow coming from a fan or similar source, the spark ignites the oil droplets in the spray. A combustion chamber is used to contain the flame and flue gases are directed through a heat exchanger to a chimney or similar exhaust. The heat of the flue gases is transferred in heat exchanger and a fan circulates a separate stream of air through the heat exchanger and throughout the building, such as a house, that the furnace is sued to heat, typically through a network of duct piping. Colder air in the building is returned to the furnace either through an air return system, typically a separate network of cold air ducts or a central return duct located near the center of the building or house, which is then passed through the heat exchanger to again to be warmed and circulated back through the living space of the house.

**[0134]** The invention provides a method of operating a heating device, such as those described above, comprising the steps of: (I) supplying to said heating device any of the heating oil compositions, including any of the quaternary ammonium salts, described above.

**[0135]** The invention also provides for the use of any of the quaternary ammonium salts described above as a soot modifiers and/or depositor control additives in any of the heating oil compositions described above and/or in any heating oil application.

**[0136]** As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, 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. As used herein, the term "hydrocarbonyl group" or "hydrocarbonyl substituent" means a hydrocarbyl group containing a carbonyl group.

**[0137]** It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. 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

**[0138]** 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.

**[0139]** A set of quaternary ammonium salts are prepared as described in the examples below.

### Example Q-1

**[0140]** Polyisobutylene succinic anhydride (100 pbw), (which itself is prepared by reacting 1000 number average molecular weight high vinylidene polyisobutylene and maleic anhydride at elevated temperatures), is heated to 80° C. and is charged to a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system. The reaction vessel is heated to 100° C. Dimethylaminopropylamine (10.9 pbw) is charged to the reaction, maintaining the batch temperature below 120° C., over an 8 hour period. The reaction mixture is then heated to 150° C. and maintained at temperature for 4 hours, resulting in a non-quaternized succinimide detergent.

**[0141]** A portion of the non-quaternized succinimide detergent (100 pbw) is then charged to a similar reaction vessel. Acetic acid (5.8 pbw) and 2-ethylhexanol (38.4 pbw) are added to the vessel and the mixture is stirred and heated to 75° C. Propylene oxide (8.5 pbw) is added to the reaction vessel over 4 hours, holding the reaction temperature at 75° C. The batch is held at temperature for 4 hours. The resulting product contains a quaternized succinimide detergent.

### Example Q-2

**[0142]** A non-quaternized succinimide detergent is prepared from a mixture of polyisobutylene succinic anhydride, as described above, (100 pbw) and diluent oil—pilot 900 (17.6 pbw) which are heated with stirring to 110° C. under a nitrogen atmosphere. Dimethylaminopropylamine (DMAPA, 10.8 pbw) is added slowly over 45 minutes maintaining batch temperature below 115° C. The reaction temperature is increased to 150° C. and held for a further 3 hours. The resulting compound is a DMAPA succinimide non-quaternized detergent. A portion of this non-quaternized succinimide detergent (100 pbw) is heated with stirring to 90° C. Dimethyl sulfate (6.8 pbw) is charged to the reaction vessel and stirring is resumed at 300 rpm under a nitrogen blanket. The resulting exotherm raises the batch temperature to ~100° C. The reaction is maintained at 100° C. for 3 hours before cooling back and decanting. The resulting product contains a dimethyl sulfate derived quaternary ammonium salt.

### Example Q-3

**[0143]** An apparatus suitable to handle chlorine and hydrogen chloride gas (glass reactor, glass stirrer, PTFE joints, glass thermowell for thermocouple) is connected to sodium hydroxide scrubbers. The glass vessel is charged with low vinylidene 1000 Mn polyisobutylene (PIB, 100 grams) and is heated to 110-120° C. Chlorine (70 grams) is bubbled into the reactor over 7 hours. The reaction mixture is then sparged with nitrogen at 110-120° C. overnight to remove HCl.

**[0144]** The resultant PIB chloride is transferred to an autoclave and the autoclave is sealed. For every mole (~1030 g) of PIB chloride, 1 mole of gaseous dimethylamine (DMA, 45 g) is added and the reaction is heated to 160-170° C. and held for 8 hours, or until no further reduction in pressure is seen. The reaction is cooled to room temperature and the pressure is released. Enough Solvesso™ 150 solvent is added to make a 70% w/w actives solution and the reaction is stirred until homogenous. The resultant polyisobutene-dimethylamine (PIB-DMA) solution is transferred to a separating funnel and washed twice with 2M sodium hydroxide solution, to remove HCl and NaCl. After separation, the product is dried over MgSO4 and is filtered through a Celite™ pad.

**[0145]** The resultant PIB-DMA solution (41 grams of the 70% active solution) is charged to a glass reaction vessel and stirred at room temperature. Dimethyl sulphate (3.3 grams) is added dropwise over one minute to provide the quaternary ammonium salt. The mixture is stirred at room temperature for 1 hour under a nitrogen blanket and is sampled and titrated against bromocresol green indicator. The resulting compound is a quaternary ammonium salt detergent of a polyalkene-substituted amine.

### Example Q-4

**[0146]** Alkylated phenol (800 grams), which itself is prepared from 1000 Mn polyisobutylene, and SO-44 diluent oil (240 grams) is charged to a reaction vessel matching the description above. A nitrogen blanket is applied to the vessel and the mixture is stirred at 100 rpm. To this mixture, Formalin (55.9 grams) is added (dropwise) over 50 minutes. After which, dimethylamine (DMA, 73.3 grams) is added (dropwise) over the next 50 minutes. The mixture is heated to 68° C. and held for one hour. The mixture is then heated to 106° C. and held for a further 2 hours. The temperature of the mixture is then increased to 130° C. and held for 30 minutes before allowing the mixture to cool to ambient temperature. The mixture is purified by vacuum distillation (at 130° C. and −0.9 bar) to remove any remaining water, resulting in a DMA Mannich.

**[0147]** The DMA Mannich (1700 grams) is added to a reaction vessel. Styrene oxide (263 grams), acetic acid (66 grams) and methanol (4564 grams) are added to the vessel and the mixture is heated with stirring to reflux (~75° C.) for 6.5 hours under a nitrogen blanket. The reaction is purified by vacuum distillation (at 30° C. and −0.8 bar). The resulting compound is a Mannich quaternary ammonium salt detergent.

### Example Q-5

**[0148]** Polyisobutylene succinic anhydride (500 g), which itself is prepared by reacting 1000 number average molecular weight high vinylidene polyisobutylene and maleic anhydride, is heated to 70° C. and charged to a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to subline addition pipe, nitrogen line and thermocouple/temperature controller system. Heptane (76.9 grams) is added to the reaction vessel and then dimethylaminopropylamine (52.3 g) is added over time, holding the reaction temperature at 70° C. Once the addition is complete, the reaction vessel is held at 70° C. for 1 hour. The resulting product, a non-quaternized succinamide detergent, is cooled and collected.

**[0149]** The resulting non-quaternized succinamide detergent (470 g), is charged to a 2-liter round bottom flange flask with water condenser attached. 2-ethylhexanol (180.6 g) is added to the flask and the mixture is stirred with an overhead stirrer and heated to 55° C. under a nitrogen blanket. Propylene oxide (40.2 g) is then added to the reaction vessel via syringe pump over 4 hours, holding the reaction temperature at 55° C. The batch is held at temperature for 16 hours. The product, which is primarily a quaternized succinamide detergent, is cooled and collected.

### Example Q-6

**[0150]** 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, 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 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.

**[0151]** 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 described above, 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 90° 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.

### Example Q-7

**[0152]** 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 $cm^{-1}$.

**[0153]** 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 described above, 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 90° 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 Set 1

**[0154]** A set of compositions are prepared for evaluation in the DGMK 570-2 Light Box Test. This test method is used to evaluate the storage stability of a heating oil composition.

**[0155]** For storage stability the sample is passed through a membrane filter, and then the oil sample is exposed to five artificial light sources (light box) for 24 hours in the presence of a copper wire, and subsequently again filtered through a membrane filter. The filter residue is washed, dried, and weighed in mg/kg as "filtratable ageing residue". The residue, which remained in the ageing vessel and on the copper wire, is dissolved in a solvent (4.5) and transferred into a vessel for evaporation. After evaporation of the solvent and drying, this residue is weighed in mg/kg as "not filtratable ageing residue". The sum of filtratable and not filtratable ageing residues is reported in mg/kg as "storage sediment". The lower the storage sediment, the better the storage stability of the composition.

**[0156]** A set of additive packages are prepared using a conventional additive package. Two of the packages also contain a conventional succinimide dispersant made from polyisobutylene succinic anhydride, which itself is prepared by reacting 1000 number average molecular weight high vinylidene polyisobutylene and maleic anhydride, and a polyalkylene polyamine. Two of the packages also contain a succinimide quaternary ammonium salt similar to that described in Example Q-1 above. All of the additive packages contain identical amounts of an alcohol, a phenolic antioxidant, an alkaryl amine antioxidant, a triazole metal deactivator, a polyisobutylene succinic acid, and a demulsifier, with the balance being made up with a petroleum naphtha solvent. One set of examples also includes an additional antioxidant booster. The formulations of the additive packages are summarized below.

TABLE 1

Additive Package Sample[1]

| | Ex A Comparative | Ex B Inventive | Ex C Comparative | Ex D Inventive |
|---|---|---|---|---|
| Additive Package[2] | 85% | 85% | 85% | 85% |
| Conventional Succinimide | 15% | 0% | 15% | 0% |
| Quaternary Ammonium Salt | 0% | 4.5% | 0% | 4.5% |
| Additional Solvent[3] | 0% | 10.5% | 0% | 10.5% |
| Antioxidant Booster | 0% | 0% | 2% | 2% |

[1] All values are percent by weight.

[2] The additive package used in each of the examples is identical.

[3] The additional solvent added here is petroleum naphtha solvent to make up for the reduced treat rate of the quaternary ammonium salt.

**[0157]** Each of the additive package examples were treated into fuels for testing in the DGMK 570-2 Light Box Test described above. One set of samples was treated at 500 ppm into an un-additized reference home heating oil (Fuel A). One set of samples was treated at 500 ppm into a fuel mixture that was 5 percent by weight soy methyl ester (SME) and 95 percent by weight of the same un-additized reference home heating oil used in the other example set (Fuel B). The results obtained are summarized below.

TABLE 2

Test Results[1]

| | Ex A Comparative | Ex B Inventive | Ex C Comparative | Ex D Inventive |
|---|---|---|---|---|
| In Fuel A at 500 ppm | 177 | 119 | 92 | 82 |
| In Fuel B at 500 ppm | 113 | 80 | 26 | 24 |

[1] Reported values are storage sediment, measured in mg/kg, which is the sum of filtratable and not filtratable ageing residues.

**[0158]** The results show that the heating oil compositions of the invention give improved storage stability over the comparative heating oil compositions that use a conventional additive in place of the described quaternary ammonium salts.

**[0159]** 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 heating oil composition comprising:

(A) a heating oil; and

(B) a quaternary ammonium salt detergent;

wherein the detergent comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen.

**2**. The composition of claim **1** wherein component (i), the compound comprising at least one tertiary amino group, comprises:

(a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent wherein the condensation product has at least one tertiary amino group;

(b) a polyalkene-substituted amine having at least one tertiary amino group;

(c) a Mannich reaction product having at least one tertiary amino group, wherein the Mannich reaction product is derived from a hydrocarbyl-substituted phenol, an aldehyde, and an amine;

(d) a compound containing at least one amide group and at least one tertiary amine functionality;

(e) a compound containing at least one ester group and at least one tertiary amino group; or

(f) any combination thereof.

**3**. The composition of claim **1** wherein component (i), the compound comprising at least one tertiary amino group, comprises the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and further having at least one tertiary amino group; and

wherein the hydrocarbyl-substituted acylating agent is polyisobutylene succinic anhydride and the compound having an oxygen or nitrogen atom capable of condensing with said acylating agent is dimethylaminopropylamine, N-methyl-1,3-diaminopropane, N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine, N,N-dimethyl-aminoethylamine, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetraamine, tetraethylenepentaamine, pentaethylenehexaamine, hexamethylenetetramine, and bis(hexamethylene)triamine.

**4**. The composition of claim **1** wherein component (i), the compound comprising at least one tertiary amino group, comprises a polyalkene-substituted amine having at least one tertiary amino group;

wherein the polyalkene substituent of the polyalkene-substituted amine is derived from polyisobutylene; and

wherein the polyalkene-substituted amine has a number average molecular weight of about 500 to about 3000.

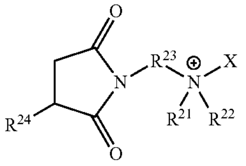
**5**. The composition of claim **1** wherein component (i), the compound comprising at least one tertiary amino group, comprises a Mannich reaction product having a tertiary amino group, said Mannich reaction product being prepared from the reaction of a hydrocarbyl-substituted phenol, an aldehyde, and an amine;

wherein the hydrocarbyl substituent of the hydrocarbyl-substituted phenol of component (a) is a polyolefin having a number average molecular weight of 400 to 3,000;

wherein the aldehyde of component (a) is a formaldehyde or a reactive equivalent thereof; and

wherein the amine of component (a) is selected from the group consisting of dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine, dibutylamine, and mixtures thereof.

**6**. The composition of claim **1** wherein the quaternary ammonium salt comprises a cation represented by the following formula:



wherein:

$R^{21}$ is a hydrocarbyl group containing from 1 to 10 carbon atoms;

$R^{22}$ is a hydrocarbyl group 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 50 to 150 carbon atoms; and

X is a group derived from the quaternizing agent.

**7**. The composition of claim **1** wherein component (ii), the quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, comprises:

(a) dialkyl sulfates;

(b) benzyl halides;

(c) hydrocarbyl substituted carbonates;

(d) hydrocarbyl epoxides;

(e) esters of carboxylic acids and/or polycarboxylic acids;

(f) any combination thereof;

wherein the quaternizing agent may optionally be used in combination with an acid.

**8**. A method of operating a heating device comprising the steps of:

I. Supplying to said heating device a heating oil composition comprising (A) a heating oil; and (B) a quaternary ammonium salt;

wherein the quaternary ammonium salt detergent comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen.

**9**. The method of claim **8** wherein component (i), the compound comprising at least one tertiary amino group, comprises:

(a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent wherein the condensation product has at least one tertiary amino group;
(b) a polyalkene-substituted amine having at least one tertiary amino group;
(c) a Mannich reaction product having at least one tertiary amino group, wherein the Mannich reaction product is derived from a hydrocarbyl-substituted phenol, an aldehyde, and an amine;
(d) a compound containing at least one amide group and at least one tertiary amine functionality;
(e) a compound containing at least one ester group and at least one tertiary amino group; or
(f) any combination thereof.

**10**. The method of claim **9** wherein component (ii), the quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, comprises:

(a) dialkyl sulfates;
(b) benzyl halides;
(c) hydrocarbyl substituted carbonates;
(d) hydrocarbyl epoxides;
(e) esters of carboxylic acids and/or polycarboxylic acids;
(f) any combination thereof;

wherein the quaternizing agent may optionally be used in combination with an acid.

**11**. The use of a quaternary ammonium salt as a soot modifier in a heating oil composition;

wherein the quaternary ammonium salt comprises the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen.

**12**. The use of claim **11** wherein component (i), the compound comprising at least one tertiary amino group, comprises:

(a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent wherein the condensation product has at least one tertiary amino group;
(b) a polyalkene-substituted amine having at least one tertiary amino group;
(c) a Mannich reaction product having at least one tertiary amino group, wherein the Mannich reaction product is derived from a hydrocarbyl-substituted phenol, an aldehyde, and an amine;
(d) a compound containing at least one amide group and at least one tertiary amine functionality;
(e) a compound containing at least one ester group and at least one tertiary amino group; or
(f) any combination thereof.

**13**. The use of claim **11** wherein component (ii), the quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, comprises:

(a) dialkyl sulfates;
(b) benzyl halides;
(c) hydrocarbyl substituted carbonates;
(d) hydrocarbyl epoxides;
(e) esters of carboxylic acids and/or polycarboxylic acids;
(f) any combination thereof;

wherein the quaternizing agent may optionally be used in combination with an acid.

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