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(54) **USE OF EPOXIDE QUATERNIZED QUATERNARY AMMONIUM SALTS**

VERWENDUNG EPOXIDQUATERNIERTER QUATERNÄRER AMMONIUMSALZE

UTILISATION DE SELS D'AMMONIUM QUATERNAIRES FONCTIONNALISÉS PAR DES AGENTS
DE QUATERNISATION ÉPOXYDE

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(73) Proprietor: **The Lubrizol Corporation**
Wickliffe, OH 44092-2298 (US)

(72) Inventors:

- **ADAMS, Paul E.**
Wickliffe, Ohio 44092-2298 (US)
- **BUSH, James H.**
Wickliffe, Ohio 44092-2298 (US)

• **GREENFIELD, Hannah**

Derby
Derbyshire DE56 1QN (GB)

• **STEVENSON, Paul R.**

Derby
Derbyshire DE56 1QN (GB)

• **MORETON, David J.**

Belper
Derby Derbyshire DE56 1QN (GB)

(74) Representative: **D Young & Co LLP**
120 Holborn
London EC1N 2DY (GB)

(56) References cited:

EP-A1- 2 862 916	EP-A1- 2 862 917
WO-A1-2013/017886	WO-A1-2013/017889
WO-A1-2014/066344	US-A1- 2012 010 112
US-A1- 2013 312 318	

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DescriptionFIELD OF THE INVENTION

5 **[0001]** The present technology is related to quaternary ammonium salts prepared with alcohol functionalized epoxide quaternizing agents, and the use of such quaternary ammonium salts in fuel compositions to improve the water shedding performance of the composition.

BACKGROUND OF THE INVENTION

10 **[0002]** Deposit formation in diesel fuel injector nozzles is highly problematic, resulting in incomplete diesel combustion, and therefore power loss and misfiring. Traditionally, polyisobutylene succinimide detergents have been used to inhibit injector fouling, but these materials have shown poor efficacy in modern engines. A new class of compounds based on quaternized polyisobutylene succinimides has been shown to provide improved detergency performance in both the
15 traditional and modern diesel engines.

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

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

[0005] US 2013/0312318 A1 discloses a method for improving or boosting separation of water from fuel oil comprising a first additive having detergent action.

SUMMARY OF THE INVENTION

30 **[0006]** We have now found that quaternary ammoniums salts prepared with alcohol functionalized epoxides, (herein referred to as "epoxide quats") result in quaternary ammonium salts that, when blended into diesel fuel, provide improved demulsification performance compared to quaternary ammonium salts prepared with other epoxides.

[0007] Thus, in one aspect the present technology provides a composition comprising an epoxide quat prepared with alcohol functionalized epoxides,
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[0008] The epoxide quat itself is the reaction product of (a) a quaternizable compound and (b) a quaternizing agent comprising alcohol functionalized epoxides,

[0009] The quaternizable compound is the reaction product of (i) a hydrocarbyl-substituted acylating agent, and (ii) a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with the hydrocarbyl-substituted
40 acylating agent, and further having at least one quaternizable amino group. The hydrocarbyl-substituent has a number average molecular weight (M_n) of from 100 to 5000 as measured using gel permeation chromatography (GPC) based on a polystyrene calibration standard.

[0010] In an embodiment, the quaternizable amino group can be a primary, secondary or tertiary amino group. The hydrocarbyl-substituted acylating agent comprises at least one polyisobutenyl succinic anhydride or polyisobutenyl
45 succinic acid.

[0011] In some embodiments, the reaction to prepare the quaternizable compound of (a) can be carried out at a temperature of greater than 80 or 90 or 100 °C. In some embodiments, water of reaction can be removed. In some
50 embodiments, the reaction to prepare the quaternizable compound of (a) can be carried out at a temperature of less than 80°C.

[0012] In an embodiment, the epoxide quat is an imide containing quaternary ammonium salt. In an embodiment, the epoxide quat is an amide or ester containing quaternary ammonium salt.

[0013] The quaternizing agent comprises, consists of, or consists essentially of alcohol functionalized epoxides. In further embodiments, the quaternizing agent can comprise, consist of, or consist essentially of glycidol.

[0014] In some embodiments, the quaternizing agent can be employed in the presence of a protic solvent. In some
55 embodiments, the quaternizing agent can be employed in the presence of 2-ethylhexanol, water, or mixtures thereof. In some embodiments, the quaternizing agent can be employed in the presence of an acid. In some embodiments, the quaternizing agent can be employed in the presence of an acid separate from the acid group present on the acylating agent. In some embodiments, the quaternizing agent can be employed in the presence of the acid group present in the

structure of the acylating agent.

[0015] In some embodiments, the compositions described above can further include at least one other additive. In some instances, the at least one other additive can be a detergent, a demulsifier, or a mixture thereof. In some instances the at least one other additive can be at least one hydrocarbyl-substituted succinic acid. In some instances, the at least one other additive can be at least one hydrocarbyl-substituted quaternary ammonium salt. In some instances where the at least one other additive is a non-quaternized or quaternized hydrocarbyl-substituted succinic acid, the hydrocarbyl-substituent can be a polyisobutylene having a number average molecular weight (M_n) of from about 100 to about 5000. In an embodiment, the at least one other additive can be at least one Mannich compound.

[0016] A further aspect of the present technology includes a composition having an epoxide quat as described herein, and further having a fuel that is liquid at room temperature. In some embodiments the fuel can be a diesel fuel.

[0017] A further embodiment of the present technology provides a method of improving water shedding, or demulsification, performance of a fuel composition. The method includes employing in a fuel, which is liquid at room temperature, a composition containing an epoxide quat as described herein. Also provided is the use of a composition containing epoxide quat as described herein, to provide improved water shedding or demulsification performance in a fuel that is liquid at room temperature.

[0018] A method of improving water shedding performance of a gasoline or diesel fuel composition is also disclosed. The method may comprise employing a composition comprising an epoxide quat as described above. The epoxide quat may be added to the fuel in an amount ranging from 5 to 1000 ppm by weight based on a total weight of the fuel composition.

BRIEF DESCRIPTION OF THE FIGURES

[0019]

FIG. 1 shows the demulsification test results of an embodiment of the disclosed technology.

FIG. 2 shows the CEC F-23-01 XUD-9 test results at 10 ppm of an embodiment of the disclosed technology.

FIG. 3 shows the CEC F-23-01 XUD-9 test results at 30 ppm of an embodiment of the disclosed technology.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The invention is set out in the appended set of claims. Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0021] One aspect of the current technology relates to a composition of an imide containing quaternary ammonium salt. The quaternary ammonium salt (herein referred to as "epoxide quats") is prepared with alcohol functionalized epoxides.

Epoxide Quats

[0022] The production of a quaternary ammonium salt generally results in a mixture of compounds including a quaternary ammonium salt or salts, and this mixture may be difficult to define apart from the process steps employed to produce the quaternary ammonium salt. Further, the process by which a quaternary ammonium salt is produced can be influential in imparting distinctive structural characteristics to the final quaternary ammonium salt product that can affect the properties of the quaternary ammonium salt product. Thus, the epoxide quats of the present technology is described as a reaction product of (a) a quaternizable compound, and (b) a quaternizing agent. As used herein, reference to epoxide quat(s) includes references to the mixture compounds including a quaternary ammonium salt or salts prepared with alcohol functionalized epoxides, as well as referring to the quaternary ammonium salt itself.

[0023] The quaternizable compound of (a) employed to prepare the epoxide quat is itself the reaction product of (i) a hydrocarbyl-substituted acylating agent, comprising at least one of polyisobutylene succinic anhydride or polyisobutylene succinic acid, and (ii) a

nitrogen containing compound. The hydrocarbyl-substituted acylating agent of (a)(i) is an acylating agent functionalized with a hydrocarbyl-substituent having a number average molecular weight of 100 to 5000.

[0024] The number average molecular weight of the materials described herein is measured using gas permeation chromatography (GPC) using a Waters GPC 2000 equipped with a refractive index detector and Waters Empower™ data acquisition and analysis software. The columns are polystyrene (PLgel, 5 micron, available from Agilent/Polymer Laboratories, Inc.). For the mobile phase, individual samples are dissolved in tetrahydrofuran and filtered with PTFE filters before they are injected into the GPC port.

Waters GPC 2000 Operating Conditions:**[0025]**

- 5 Injector, Column, and Pump/Solvent compartment temperatures: 40° C
 Autosampler Control: Run time: 40 minutes
 Injection volume: 300 microliter
 Pump: System pressure: ~90 bars (Max. pressure limit: 270 bars, Min. pressure limit: 0 psi)
 Flow rate: 1.0 ml/minute
 10 Differential Refractometer (RI): Sensitivity: -16; Scale factor: 6

[0026] Examples of quaternary ammonium salts and methods for preparing the same are described in the following patents, US 4,253,980, US 3,778,371, US 4,171,959, US 4,326,973, US 4,338,206, US 5,254,138, and US 7,951,211.

- 15 **[0027]** Details regarding the quaternizable compound, and specifically, the hydrocarbyl-substituted acylating agent and the nitrogen containing compound, as well as the quaternizing agent, are provided below.

The Hydrocarbyl Substituted Acylating Agent

- 20 **[0028]** The hydrocarbyl substituted acylating agent employed to prepare the quaternizable compound is the reaction product of the precursor to the hydrocarbyl-substituent, which is maleic acid or maleic anhydride,

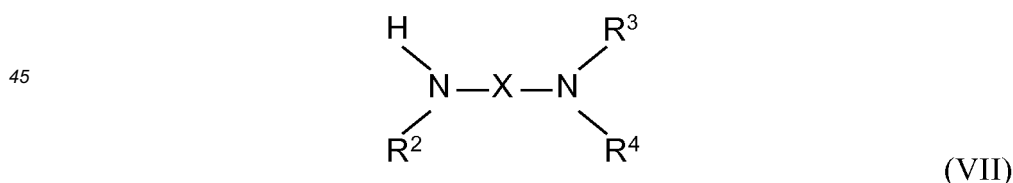
- [0029]** The hydrocarbyl group has a number average molecular weight (M_n) of from 100 or 300 to 5000, or from about 500 to about 2500. The M_n of the hydrocarbyl group can also be from about 1300 to about 3000. The M_n of the hydrocarbyl-substituent can also be from 1500 to 2800 or 2900, or from 1700 to 2700, or from 1900 to 2600, or 2000 to 2500. In an embodiment, the M_n can be from about 300 to about 750. The M_n of the hydrocarbyl-substituent can also be from about 350 to 700, and in some cases from 400 to 600, or 650. In yet other embodiments the M_n of the hydrocarbyl-substituent can also be 550, or 1000, or 2300. In yet another embodiment, the hydrocarbyl-substituent may have a number average molecular weight of 1000 to 2300.

- 25 **[0030]** In other embodiments, the hydrocarbyl-substituted acylating agent may be a "conventional" vinylidene polyisobutylene (PIB) wherein less than 20% of the head groups are vinylidene head groups as measured by nuclear magnetic resonance (NMR). Alternatively, the hydrocarbyl-substituted acylating agent may be a mid-vinylidene PIB or a high-vinylidene PIB. In mid-vinylidene PIBs, the percentage of head groups that are vinylidene groups can range from greater than 20% to 70%. In high-vinylidene PIBs, the percentage of head groups that are vinylidene head groups is greater than 70%.

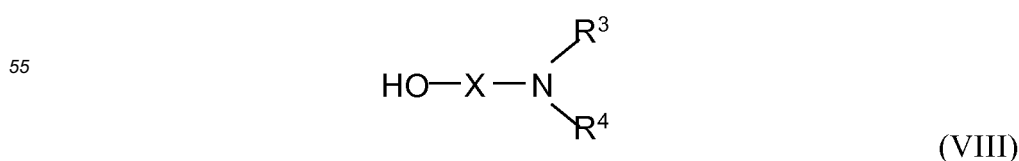
35 Nitrogen Containing Compound

- [0031]** The composition of the present technology contains a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with the acylating agent and further having a quaternizable amino group. A quaternizable amino group is any primary, secondary or tertiary amino group on the nitrogen containing compound that is available to react with a quaternizing agent to become a quaternary amino group.

40 **[0032]** In one embodiment, the nitrogen containing compound can be represented by the following formulas:



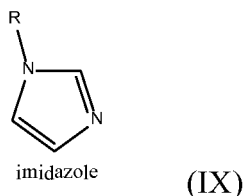
- 50 wherein X is an alkylene group containing 1 to 4 carbon atoms; R_2 may be a H or a hydrocarbyl group; and R_3 and R_4 are hydrocarbyl groups.



wherein X is a alkylene group containing about 1 to about 4 carbon atoms; R3 and R4 are hydrocarbyl groups.

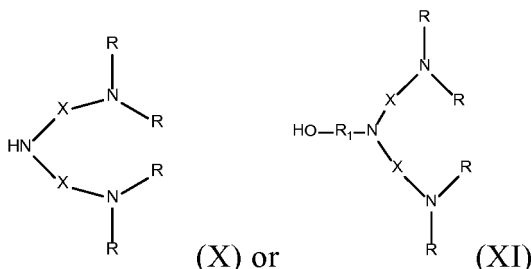
[0033] Examples of the nitrogen containing compound capable of reacting with the acylating agent can include, but are not limited to, dimethylaminopropylamine, N,N-dimethyl-aminopropylamine, N,N-diethyl-aminopropylamine, N,N-dimethylaminoethylamine ethylenediamine, 1,2-propylenediamine, 1,3-propylene diamine, the isomeric butylenediamines, pentanediamines, hexanediamines, heptanediamines, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetraamine, tetraethylenepentaamine, pentaethylenehexaamine, hexamethylenetetramine, and bis(hexamethylene) triamine, the diaminobenzenes, the diaminopyridines or mixtures thereof. The nitrogen containing compounds capable of reacting with the acylating agent and further having a quaternizable amino group can further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine. Additional nitrogen containing compounds capable of reacting with the acylating agent and having a quaternizable amino group include alkanolamines including but not limited to triethanolamine, trimethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, N,N,N-tris(hydroxyethyl)amine, N,N,N-tris(hydroxymethyl)amine, N,N-dimethylethanolamine, N,N-diethylethanolamine, 2-(diisopropylamino)ethanol, 2-(dibutylamino)ethanol, 3-dimethylamino-1-propanol, 3-diethylamino-1-propanol, 1-dimethylamino-2-propanol, 1-diethylamino-2-propanol, 2-dimethylamino-2-methyl-1-propanol, 5-dimethylamino-2-propanol, 2-[2-(dimethylamino)ethoxy]-ethanol, 4-methyl-2-(piperidino methyl)phenol, 1-benzyl-3-pyrrolidinol, 1-benzylpyrrolidine-2-methanol, 2,4,6-tri(dimethylaminomethyl)phenol, dialkoxylated amines such as Ethermeen T12. In some embodiments, the nitrogen containing compound excludes dimethylaminopropylamine.

[0034] In one embodiment, the nitrogen containing compound can be an imidazole, for example, as represented by the following formula:



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

[0035] In one embodiment, the nitrogen containing compound can be represented by at least one of formulas X or XI:



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

Quaternizable Compound

[0036] The hydrocarbyl substituted acylating agents and nitrogen containing compounds described above are reacted together to form a quaternizable compound. Methods and process for reacting the hydrocarbyl substituted acylating agents and nitrogen containing compounds are well known in the art.

[0037] In embodiments, the reaction between the hydrocarbyl substituted acylating agents and nitrogen containing compounds can be carried out at temperatures of greater than about 80 °C, or 90 °C, or in some cases 100 °C, such as between 100 and 150 or 200 °C, or 125 and 175 °C. In yet another embodiments the reaction between the hydrocarbyl substituted acylating agents and the nitrogen containing compounds may be carried out at temperatures less than 80 °C, or 70 °C, or 60 °C, and in some cases between 40 °C and 80 °C. At the foregoing temperatures water may be produced during the condensation, which is referred to herein as the water of reaction. In some embodiments, the water

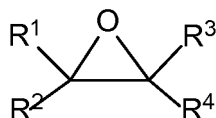
of reaction can be removed during the reaction, such that the water of reaction does not return to the reaction and further react.

[0038] The hydrocarbyl substituted acylating agents and nitrogen containing compounds may be reacted at a ratio of 1:1, but the reaction may also contain the respective reactants (i.e., hydrocarbyl substituted acylating agent:nitrogen containing compound) in ratios from 3:1 to 1:1.2, or from 2.5:1 to 1:1.1, and in some embodiments from 2:1 to 1:1.05.

Quaternizing agent

[0039] The quaternary ammonium salt is formed when the quaternizable compound, that is, the reaction products of the hydrocarbyl substituted acylating agent and nitrogen containing compounds described above, are reacted with a quaternizing agent. Suitable quaternizing agents include, alcohol functionalized epoxides.

[0040] Exemplary epoxides, can be represented by the following formula:



(VIII)

[0041] Exemplary alcohol functionalized epoxides can include those of formula VIII where R^1 , R^2 , R^3 and R^4 can be independently H or a hydroxyl containing hydrocarbyl group. In an embodiment, hydroxyl containing hydrocarbyl group can contain from 2 to 32, or from 3 to 28, or even from 3 to 24 carbon atoms. Exemplary alcohol functionalized epoxide derivatives can include for example, glycidol and the like.

[0042] In some embodiments the quaternizing agent can be employed in combination with an acid. The acid used with the quaternizing agent may be a separate component, such as acetic acid, propionic acid, 2-ethylhexanoic acid, and the like. In other embodiments, a small amount of an acid component may be present, such as, about at <0.2 or even <0.1 moles of acid per mole of hydrocarbyl acylating agent.

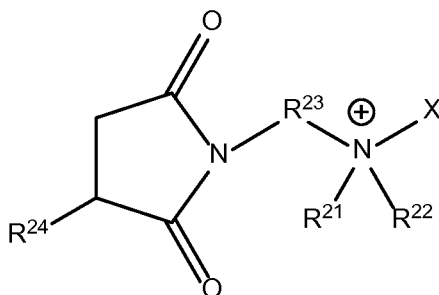
[0043] In certain embodiments the molar ratio of the condensation compound to quaternizing agent is 1:0.1 to 2, or 1:1 to 1.5, or 1:1 to 1.3.

[0044] In some embodiments, the quaternizing agent can be employed in the presence of a protic solvent, such as, for example, 2-ethylhexanol, water, and combinations thereof. In some embodiments, the quaternizing agent can be employed in the presence of an acid. In yet another embodiment, the quaternizing agent can be employed in the presence of an acid and a protic solvent. In some embodiments, the acid can be an acid component in addition to the acid group present in the structure of the acylating agent. In further embodiments the reaction can be free of, or essentially free of, any additional acid component other than the acid group present in the structure of the acylating agent. By "free of" it is meant completely free, and by "essentially free" it is meant an amount that not materially affect the essential or basic and novel characteristics of the composition, such as, for example, less than 1% by weight.

Structure

[0045] While the process to prepare the epoxide quats can produce a mixture that is not readily definable apart from the process steps, certain structural components may be expected in some circumstances.

[0046] In some embodiments the epoxide quats can comprise, consist essentially of, or consist of a cation represented by the following formula:

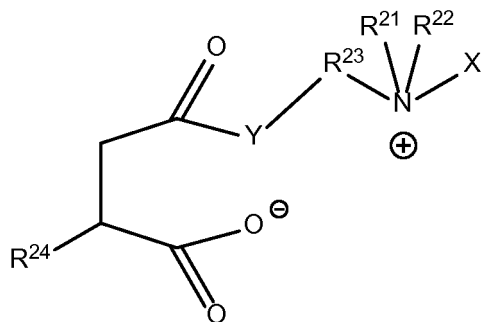


(XIV)

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 5 to 400 carbon atoms, or from 15 or 25 to 300 or 350 carbon atoms, or from 50 or 120 to 250 carbon atoms, or from 135 to 200 carbon atoms; and X is a group derived from the quaternizing agent. In some embodiments, R^{24} can be a hydrocarbyl group containing from 92 to 215 carbon atoms, or from 107 to 200 or 210 carbon atoms, or from 120 to 195 carbon atoms, or from 135 to 190 or from 140 to 180 or 185 carbon atoms, or a hydrocarbyl group containing from 20 to 55 carbon atoms, or from 25 to 50, or from 28 to 43 or 47 carbon atoms.

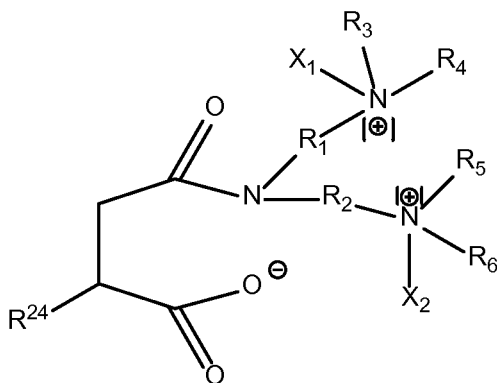
[0047] In some embodiments the epoxide quats can comprise, consist essentially of, or consist of a cation represented by the following formula:



(XV)

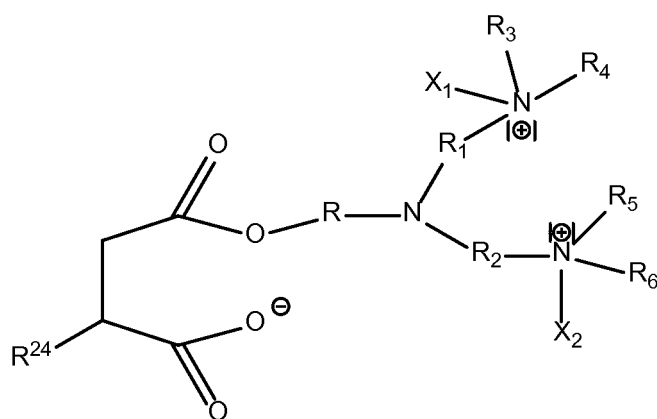
wherein: R^{21} and R^{22} are hydrocarbyl groups containing from 1 to 10 carbon atoms; R^{23} is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^{24} is a hydrocarbyl group containing from 5 to 400 carbon atoms, or from 15 or 25 to 300 or 350 carbon atoms, or from 50 or 120 to 250 carbon atoms, or from 135 to 200 carbon atoms; X is a group derived from the quaternizing agent; and Y is oxygen or nitrogen. In some embodiments, R^{24} can be a hydrocarbyl group containing from 92 to 215 carbon atoms, or from 107 to 200 or 210 carbon atoms, or from 120 to 195 carbon atoms, or from 135 to 190 or from 140 to 180 or 185 carbon atoms, or a hydrocarbyl group containing from 20 to 55 carbon atoms, or from 25 to 50, or from 28 to 43 or 47 carbon atoms.

[0048] In some embodiments the epoxide quats can comprise, consist essentially of, or consist of a cation represented by the following formulas:



(XVI)

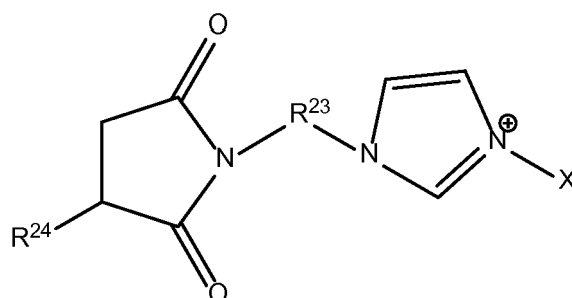
or



(XVII)

wherein: R can be a C₁ to C₆ alkyl group; R₁ and R₂, individually, can be a C₁ to C₆ hydrocarbyl group, for example a C₁, C₂, or C₃ alkyl group; R₃, R₄, R₅ and R₆, individually, can be hydrogen or a C₁ to C₆ hydrocarbyl group, such as, for example, a C₁, C₂, or C₃ alkyl group; R²⁴ is a hydrocarbyl group containing from 5 to 400 carbon atoms, or from 15 or 25 to 300 or 350 carbon atoms, or from 50 or 120 to 250 carbon atoms, or from 135 to 200 carbon atoms; X₁ and X₂, individually, can be H or a group derived from the quaternizing agent, so long as at least one of X₁ and X₂ is a group derived from the quaternizing agent. In some embodiments, R²⁴ can be a hydrocarbyl group containing from 92 to 215 carbon atoms, or from 107 to 200 or 210 carbon atoms, or from 120 to 195 carbon atoms, or from 135 to 190 or from 140 to 180 or 185 carbon atoms, or a hydrocarbyl group containing from 20 to 55 carbon atoms, or from 25 to 50, or from 28 to 43 or 47 carbon atoms.

[0049] In some embodiments the epoxide quats can comprise, consist essentially of, or consist of a cation represented by the following formula:



(XVIII)

wherein: R²³ is a hydrocarbylene group containing from 1 to 20 carbon atoms; R²⁴ is a hydrocarbyl group containing from 5 to 400 carbon atoms, or from 15 or 25 to 300 or 350 carbon atoms, or from 50 or 120 to 250 carbon atoms, or from 135 to 200 carbon atoms; and X is a group derived from the quaternizing agent. In some embodiments, R²⁴ can be a hydrocarbyl group containing from 92 to 215 carbon atoms, or from 107 to 200 or 210 carbon atoms, or from 120 to 195 carbon atoms, or from 135 to 190 or from 140 to 180 or 185 carbon atoms, or a hydrocarbyl group containing from 20 to 55 carbon atoms, or from 25 to 50, or from 28 to 43 or 47 carbon atoms.

Compositions

[0050] In one embodiment, the present technology provides a composition comprising an epoxide quat, and the use of the composition in a fuel composition to improve the water shedding performance of the fuel composition.

Fuel

[0051] The compositions can comprise a fuel which is liquid at room temperature and is useful in fueling an engine. The fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30 °C). The fuel can be a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel can be a petroleum distillate to include a gasoline as defined by EN228 or ASTM specification D4814, or a diesel fuel as defined by EN590 or ASTM specification D975. In an embodiment of the invention the fuel is a gasoline, and in other embodiments the fuel is a leaded gasoline, or a

nonleaded gasoline. In another embodiment of this invention the fuel is a diesel fuel. The hydrocarbon fuel can be a hydrocarbon prepared by a gas to liquid process to include for example hydrocarbons prepared by a process such as the Fischer-Tropsch process. The nonhydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, to include an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof.

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

[0052] Treat rates of the epoxide quats to fuel range from 5 to 1000 ppm or 5 to 500 ppm, or 10 to 250 ppm, or 10 to 150 ppm, or 15 to 100 ppm. In other embodiments the treat rate range may be from 250 to 1000 ppm, or 250 to 750 ppm, or 500 to 750 ppm or 250 ppm to 500 ppm.

Miscellaneous

[0053] The fuel compositions include the epoxide quats described above and may also include one or more additional additives. Such additional performance additives can be added to any of the compositions described depending on the results desired and the application in which the composition will be used.

[0054] Although any of the additional performance additives described herein can be used in any of the fuel compositions the following additional additives are particularly useful for fuel compositions: antioxidants, corrosion inhibitors, detergent and/or dispersant additives other than those described above, cold flow improvers, foam inhibitors, demulsifiers, lubricity agents, metal deactivators, valve seat recession additives, biocides, antistatic agents, deicers, fluidizers, combustion improvers, seal swelling agents, wax control polymers, scale inhibitors, gas-hydrate inhibitors, or any combination thereof.

[0055] Demulsifiers suitable for use with the epoxide quats of the present technology can include, but not be limited to, arylsulfonates and polyalkoxylated alcohol, such as, for example, polyethylene and polypropylene oxide copolymers and the like. The demulsifiers can also comprise nitrogen containing compounds such as oxazoline and imidazoline compounds and fatty amines, as well as Mannich compounds. Mannich compounds are the reaction products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: U.S. Pat. Nos. 3,036,003; 3,236,770; 3,414,347; 3,448,047; 3,461,172; 3,539,633; 3,586,629; 3,591,598; 3,634,515; 3,725,480; 3,726,882; and 3,980,569. Other suitable demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene oxide (EO) and propylene oxide (PO), for example including in the form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. In an embodiment there is no demulsifier present in the fuel and/or lubricant composition. The demulsifiers may be used alone or in combination. Some demulsifiers are commercially available, for example from Nalco or Baker Hughes.

[0056] Suitable antioxidants include for example hindered phenols or derivatives thereof and/or diarylamines or derivatives thereof. Suitable detergent/dispersant additives include for example polyetheramines or nitrogen containing detergents, including but not limited to PIB amine detergents/dispersants, succinimide detergents/dispersants, and other quaternary salt detergents/dispersants including polyisobutylsuccinimide-derived quaternized PIB/amine and/or amide dispersants/detergents. Suitable cold flow improvers include for example esterified copolymers of maleic anhydride and styrene and/or copolymers of ethylene and vinyl acetate. Suitable lubricity improvers or friction modifiers are based typically on fatty acids or fatty acid esters. Typical examples are tall oil fatty acid, as described, for example, in WO

98/004656, and glyceryl monooleate. The reaction products, described in U.S. Pat. No. 6,743,266 B2, of natural or synthetic oils, for example triglycerides, and alkanolamines are also suitable as such lubricity improvers. Additional examples include commercial tall oil fatty acids containing polycyclic hydrocarbons and/or rosin acids. Suitable metal deactivators include for example aromatic triazoles or derivatives thereof, including but not limited to benzotriazole. Other suitable metal deactivators are, for example, salicylic acid derivatives such as N,N'-disalicylidene-1,2-propanediamine. Suitable valve seat recession additives include for example alkali metal sulfosuccinate salts. Suitable foam inhibitors and/or antifoams include for example organic silicones such as polydimethyl siloxane, polyethylsiloxane, polydiethylsiloxane, polyacrylates and polymethacrylates, trimethyl-trifluoro-propylmethyl siloxane and the like. Suitable fluidizers include for example mineral oils and/or poly(α -olefins) and/or polyethers. Combustion improvers include for example octane and cetane improvers. Suitable cetane number improvers are, for example, aliphatic nitrates such as 2-ethylhexyl nitrate and cyclohexyl nitrate and peroxides such as di-tert-butyl peroxide.

[0057] The additional performance additives, which may be present in the fuel compositions also include di-ester, di-amide, ester-amide, and ester-imide friction modifiers prepared by reacting an α -hydroxy acid with an amine and/or alcohol optionally in the presence of a known esterification catalyst. Examples of α -hydroxy acids include glycolic acid, lactic acid, α -hydroxy dicarboxylic acid (such as tartaric acid) and/or an α -hydroxy tricarboxylic acid (such as citric acid), with an amine and/or alcohol, optionally in the presence of a known esterification catalyst. These friction modifiers, often derived from tartaric acid, citric acid, or derivatives thereof, may be derived from amines and/or alcohols that are branched, resulting in friction modifiers that themselves have significant amounts of branched hydrocarbyl groups present within it structure. Examples of suitable branched alcohols used to prepare such friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, and mixtures thereof. Friction modifiers may be present at 0 to 6 wt % or 0.001 to 4 wt %, or 0.01 to 2 wt % or 0.05 to 3 wt % or 0.1 to 2 wt % or 0.1 to 1 wt % or 0.001 to 0.01 wt %.

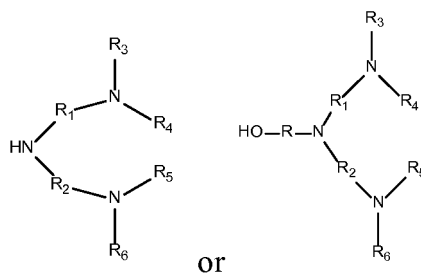
[0058] The additional performance additives may comprise a detergent/dispersant comprising a hydrocarbyl substituted acylating agent. The acylating agent may be, for example, a hydrocarbyl substituted succinic acid, or the condensation product of a hydrocarbyl substituted succinic acid with an amine or an alcohol; that is, a hydrocarbyl substituted succinimide or hydrocarbyl substituted succinate. In an embodiment, the detergent/dispersant may be a polyisobutenyl substituted succinic acid, amide or ester, wherein the polyisobutenyl substituent has a number average molecular weight of from about 100 to 5000. In some embodiments, the detergent may be a C₆ to C₁₈ substituted succinic acid, amide or ester. A more thorough description of the hydrocarbyl substituted acylating agent detergents can be found from paragraph [0017] to [0036] of U.S. Publication 2011/0219674, published September 15, 2011.

[0059] In one embodiment, the additional detergent/dispersant is a quaternary ammonium salt other than that of the present technology. Additional quaternary ammonium salts can be quaternary ammonium salts prepared from hydrocarbyl substituted acylating agents, such as, for example, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750, or polyisobutyl succinic acids anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 1000 M_n.

[0060] In an embodiment, the additional quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of 300 to 750 or 1300 to 3000 is an amide or ester. In an embodiment, the quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n or having a hydrocarbyl substituent with a number average molecular weight of from 300 to 750 is an imide.

[0061] In yet another embodiment the hydrocarbyl substituted acylating agent can include a mono-, dimer or trimer carboxylic acid with 8 to 54 carbon atoms and is reactive with primary or secondary amines. Suitable acids include, but are not limited to, the mono-, dimer, or trimer acids of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic, arachidic acid, behenic acid, lignoceric acid, cerotic acid, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, α -linolenic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, and docosahexaenoic acid.

[0062] In an embodiment the nitrogen containing compound of the additional quaternary ammonium salts is an imidazole or nitrogen containing compound of either of formulas.

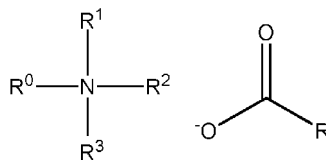


wherein R may be a C₁ to C₆ alkylene group; each of R₁ and R₂, individually, may be a C₁ to C₆ hydrocarbylene group; and each of R₃, R₄, R₅, and R₆, individually, may be a hydrogen or a C₁ to C₆ hydrocarbyl group.

[0063] In other embodiments, the quaternizing agent used to prepare the additional quaternary ammonium salts can be a dialkyl sulfate, an alkyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, a carboxylate, alkyl esters, or mixtures thereof. In some cases the quaternizing agent can be a hydrocarbyl epoxide. In some cases the quaternizing agent can be a hydrocarbyl epoxide in combination with an acid. In some cases the quaternizing agent can be a salicylate, oxalate or terephthalate. In an embodiment the hydrocarbyl epoxide is an alcohol functionalized epoxides or C₄ to C₁₄ epoxides.

[0064] In some embodiments, the quaternizing agent is multi-functional resulting in the additional quaternary ammonium salts being coupled quaternary ammoniums salts.

[0065] Additional quaternary ammonium salts include, but are not limited to quaternary ammonium salts having a hydrophobic moiety in the anion. Exemplary compounds include quaternary ammonium compounds having the formula below:



wherein R⁰, R¹, R² and R³ is each individually an optionally substituted alkyl, alkenyl or aryl group and R includes an optionally substituted hydrocarbyl moiety having at least 5 carbon atoms.

[0066] Additional quaternary ammonium salts may also include polyetheramines that are the reaction products of a polyether-substituted amine comprising at least one tertiary quaternizable amino group and a quaternizing agent that converts the tertiary amino group to a quaternary ammonium group.

[0067] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptotriazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403.

[0068] The fuel compositions may include a detergent additive, different from the disclosed epoxide quat technology. Most conventional detergents used in the field of engine lubrication obtain most or all of their basicity or TBN from the presence of basic metal-containing compounds (metal hydroxides, oxides, or carbonates, typically based on such metals as calcium, magnesium, or sodium). Such metallic overbased detergents, also referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are typically prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid such as carbon dioxide) with a mixture of an acidic organic compound (also referred to as a substrate), a stoichiometric excess of a metal base, typically in a reaction medium of an one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for the acidic organic substrate. Typically also a small amount of promoter such as a phenol or alcohol is present, and in some cases a small amount of water. The acidic organic substrate will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil.

[0069] Such conventional overbased materials and their methods of preparation are well known to those skilled in the art. Patents describing techniques for making basic metallic salts of sulfonic acids, carboxylic acids, phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. Salixarate detergents are described in U.S. patent 6,200,936. In certain embodiments, the detergent may contain a metal-containing salicylate detergent, such as an overbased calcium hydrocarbyl-substituted salicylate detergent and are described in U.S. Patents

5,688,751 and 4,627,928.

[0070] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the fuel compositions. Viscosity improvers are usually polymers, including polyisobutenes, polymethacrylates (PMA) and polymethacrylic acid esters, hydrogenated diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins. PMA's are prepared from mixtures of methacrylate monomers having different alkyl groups. The alkyl groups may be either straight chain or branched chain groups containing from 1 to 18 carbon atoms. Most PMA's are viscosity modifiers as well as pour point depressants.

[0071] Multifunctional viscosity improvers, which also have dispersant and/or antioxidant properties are known and may optionally be used in the fuel compositions. Dispersant viscosity modifiers (DVM) are one example of such multifunctional additives. DVM are typically prepared by copolymerizing a small amount of a nitrogen-containing monomer with alkyl methacrylates, resulting in an additive with some combination of dispersancy, viscosity modification, pour point depressancy and dispersancy. Vinyl pyridine, N-vinyl pyrrolidone and N,N'-dimethylaminoethyl methacrylate are examples of nitrogen-containing monomers. Polyacrylates obtained from the polymerization or copolymerization of one or more alkyl acrylates also are useful as viscosity modifiers.

[0072] Anti-wear agents may be used in the fuel compositions provide herein. Anti-wear agents can in some embodiments include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2 or 0.015 to 0.15 or 0.02 to 0.1 or 0.025 to 0.08 percent by weight phosphorus. Often the antiwear agent is a zinc dialkylthiophosphate (ZDP). For a typical ZDP, which may contain 11 percent P (calculated on an oil free basis), suitable amounts may include 0.09 to 0.82 percent by weight. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins. In some embodiments the fuel and/or lubricant compositions of the invention are free of phosphorus-containing antiwear/extreme pressure agents.

[0073] Foam inhibitors that may be useful in fuel compositions include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. The disclosed technology may also be used with a silicone-containing antifoam agent in combination with a C₅ - C₁₇ alcohol.

[0074] Pour point depressants that may be useful in fuel compositions include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0075] Metal deactivators may be chosen from a derivative of benzotriazole (typically tolyltriazole), 1,2,4-triazole, benzimidazole, 2-alkyldithiobenzimidazole or 2-alkyldithiobenzothiazole, 1-amino-2-propanol, a derivative of dimercaptotriadiazole, octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and/or a fatty acid such as oleic acid with a polyamine.. The metal deactivators may also be described as corrosion inhibitors.

[0076] Seal swell agents include sulpholene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

Fuel Compositions

[0077] In some embodiments the technology provides fuel compositions. In some embodiments, the fuel compositions comprise a majority (>50 wt%) of gasoline or a middle distillate fuel. In an embodiment, there is provided a fuel composition comprising a majority of a diesel fuel.

[0078] In yet another embodiment, the fuel composition comprises the epoxide quats of disclosed herein and a demulsifier. Demulsifiers suitable for use with the quaternary ammonium salts of the present technology can include, but not be limited to arylsulfonates and polyalkoxylated alcohol, such as, for example, polyethylene and polypropylene oxide copolymers and the like. The demulsifiers can also comprise nitrogen containing compounds such as oxazoline and imidazoline compounds and fatty amines, as well as Mannich compounds. Mannich compounds are the reaction products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: U.S. Pat. Nos. 3,036,003; 3,236,770; 3,414,347; 3,448,047; 3,461,172; 3,539,633; 3,586,629; 3,591,598; 3,634,515; 3,725,480; 3,726,882; and 3,980,569.

[0079] Other suitable demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene oxide (EO) and propylene oxide (PO), for example including in the form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. In one embodiment the fuel composition of the invention does not comprise a demulsifier.

The demulsifiers may be used alone or in combination. Some demulsifiers are commercially available, for example from Nalco or Baker Hughes. Typical treat rates of the demulsifiers to a fuel may range from 0 to 50 ppm by total weight of the fuel, or 5 to 50 ppm, or 5 to 25 ppm, or 5 to 20 ppm.

[0080] The disclosed technology may also be used with demulsifiers comprising a hydrocarbyl-substituted dicarboxylic acid in the form of the free acid, or in the form of the anhydride which may be an intramolecular anhydride, such as succinic, glutaric, or phthalic anhydride, or an intermolecular anhydride linking two dicarboxylic acid molecules together. The hydrocarbyl substituent may have from 12 to 2000 carbon atoms and may include polyisobutenyl substituents having a number average molecular weight of 300 to 2800. Exemplary hydrocarbyl-substituted dicarboxylic acids include, but are not limited to, hydrocarbyl-substituted acids derived from malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, undecanedioic, dodecanedioic, phthalic, isophthalic, terphthalic, o-, m-, or p-phenylene diacetic, maleic, fumaric, or glutaconic acids.

[0081] In another embodiment, a fuel composition comprises the epoxide quats of the present invention and an additional detergent/dispersant. Customary detergent/dispersant additives are preferably amphiphilic substances which possess at least one hydrophobic hydrocarbon radical with a number-average molecular weight of 100 to 10000 and at least one polar moiety selected from (i) Mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties; (ii) Hydroxyl groups in combination with mono or polyamino groups, at least one nitrogen atoms having basic properties; (iii) Carboxyl groups or their alkali metal or alkaline earth metal salts; (iv) Sulfonic acid groups or their alkali metal or alkaline earth metal salts; (v) Polyoxy-C₂ to C₄ alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups; (vi) Carboxylic ester groups; (vii) Moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or (viii) Moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono-or polyamines.

[0082] The hydrophobic hydrocarbon radical in the above detergent/dispersant additives which ensures the adequate solubility in the fuel, has a number-average molecular weight (M_n) of 85 to 20,000, of 100 to 10,000, or 300 to 5000. In yet another embodiment, the detergent/dispersant additives have a M_n of 300 to 3000, of 500 to 2500, of 700 to 2500, or 800 to 1500. Typical hydrophobic hydrocarbon radicals may be polypropenyl, polybutenyl and polyisobutenyl radicals, with a number average molecular weight M_n , of 300 to 5000, of 300 to 3000, of 500 to 2500, or 700 to 2500. In one embodiment the detergent/dispersant additives have a M_n of 800 to 1500.

[0083] 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(alkylene-amine). Succinimide detergents/dispersants are more fully described in U.S. patents 4,234,435 and 3,172,892. Another class of ashless dispersant is high molecular weight esters, prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0084] Nitrogen-containing detergents are the reaction products of a carboxylic acid-derived acylating agent and an amine. The acylating agent can vary from formic acid and its acylating derivatives to acylating agents having high molecular weight aliphatic substituents of up to 5,000, 10,000 or 20,000 carbon atoms. The amino compounds can vary from ammonia itself to amines typically having aliphatic substituents of up to about 30 carbon atoms, and up to 11 nitrogen atoms. Acylated amino compounds suitable for use in the present invention are those formed by the reaction of an acylating agent having a hydrocarbyl substituent of at least 8 carbon atoms and a compound comprising at least one primary or secondary amine group. The acylating agent may be a mono- or polycarboxylic acid (or reactive equivalent thereof) for example a substituted succinic, phthalic or propionic acid and the amino compound may be a polyamine or a mixture of polyamines, for example a mixture of ethylene polyamines. Alternatively the amine may be a hydroxyalkyl-substituted polyamine. The hydrocarbyl substituent in such acylating agents may comprise at least 10 carbon atoms. In one embodiment, the hydrocarbyl substituent may comprise at least 12, for example 30 or 50 carbon atoms. In yet another embodiment, it may comprise up to 200 carbon atoms. The hydrocarbyl substituent of the acylating agent may have a number average molecular weight (M_n) of 170 to 2800, for example from 250 to 1500. In other embodiments, the substituent's M_n may range from 500 to 1500, or alternatively from 500 to 1100. In yet another embodiment, the substituent's M_n may range from 700 to 1300. In another embodiment, the hydrocarbyl substituent may have a number average molecular weight of 700 to 1000, or 700 to 850, or, for example, 750.

[0085] Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde and are described in more detail in U.S. Patent 3,634,515.

[0086] A useful nitrogen containing dispersant includes the product of a Mannich reaction between (a) an aldehyde, (b) a polyamine, and (c) an optionally substituted phenol. The phenol may be substituted such that the Mannich product has a molecular weight of less than 7500. Optionally, the molecular weight may be less than 2000, less than 1500, less than 1300, or for example, less than 1200, less than 1100, less than 1000. In some embodiments, the Mannich product has a molecular weight of less than 900, less than 850, or less than 800, less than 500, or less than 400. The substituted

phenol may be substituted with up to 4 groups on the aromatic ring. For example it may be a tri or disubstituted phenol. In some embodiments, the phenol may be a mono-substituted phenol. The substitution may be at the ortho, and/or meta, and/or para position(s). To form the Mannich product, the molar ratio of the aldehyde to amine is from 4:1 to 1:1 or, from 2:1 to 1:1. The molar ratio of the aldehyde to phenol may be at least 0.75:1; or 0.75 to 1 to 4:1, or 1:1 to 4:1, or 1:1 to 2:1. To form the preferred Mannich product, the molar ratio of the phenol to amine can be at least 1.5:1, at least 1.6:1, at least 1.7:1, for example at least 1.8:1, or at least 1.9:1. The molar ratio of phenol to amine may be up to 5:1; for example it may be up to 4:1, or up to 3.5:1. Suitably it is up to 3.25:1, up to 3:1, up to 2.5:1, up to 2.3:1 or up to 2.1:1.

[0087] 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.

[0088] In an embodiment, the fuel composition can additionally comprise quaternary ammonium salts other than the epoxide quats disclosed herein. The other quaternary ammonium salts can comprise (a) a compound comprising (i) at least one tertiary amino group as described above, and (ii) a hydrocarbyl-substituent having a number average molecular weight of 100 to 5000, or 250 to 4000, or 100 to 4000, or 100 to 2500, or 3000; and (b) a quaternizing agent suitable for converting the tertiary amino group of (a)(i) to a quaternary nitrogen, as described above. The other quaternary ammonium salts are more thoroughly described in U.S. Patent Nos. 7,951,211, issued May 31, 2011, and 8,083,814, issued December 27, 2011, and U.S. Publication Nos. 2013/0118062, published May 16, 2013, 2012/0010112, published January 12, 2012, 2013/0133243, published May 30, 2013, 2008/0113890, published May 15, 2008, and 2011/0219674, published September 15, 2011, US 2012/0149617 published May 14, 2012, US 2013/0225463 published August 29, 2013, US 2011/0258917 published October 27, 2011, US 2011/0315107 published December 29, 2011, US 2013/0074794 published March 28, 2013, US 2012/0255512 published October 11, 2012, US 2013/0333649 published December 19, 2013, US 2013/0118062 published May 16, 2013, and international publications WO Publication Nos. 2011/141731, published November 17, 2011, 2011/095819, published August 11, 2011, and 2013/017886, published February 7, 2013, WO 2013/070503 published May 16, 2013, WO 2011/110860 published September 15, 2011, WO 2013/017889 published February 7, 2013, WO 2013/017884 published February 7, 2013.

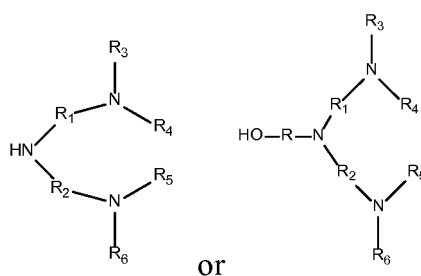
[0089] The additional quaternary ammoniums salts other than the disclosed technology can be quaternary ammoniums salts prepared from hydrocarbyl substituted acylating agents, such as, for example, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n , polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750, or polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 1000 M_n .

[0090] In an embodiment, the fuel composition comprising the epoxide quats disclosed herein can further comprise additional quaternary ammonium salts that are amides or esters. The additional amide or ester quats are prepared from the reaction of a nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of 300 to 750, or 1300 to 3000. In an embodiment, the fuel compositions can further comprise additional quaternary ammonium salts that are imides. The imide quats are prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n or, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750.

[0091] The hydrocarbyl substituted acylating agent may also be a copolymer formed by copolymerizing at least one monomer that is an ethylenically unsaturated hydrocarbon having 2 to 100 carbon atoms. The monomer may be linear, branched, or cyclic. The monomer may have oxygen or nitrogen substituents, but will not react with amines or alcohols. The monomer may be reacted with a second monomer that is a carboxylic acid or carboxylic acid derivative having 3 to 12 carbon atoms. The second monomer may have one or two carboxylic acid functional groups and is reactive with amines or alcohols. When made using this process, the hydrocarbyl substituted acylating agent copolymer has a number average molecular weight M_n of 500 to 20,000.

[0092] Alternatively, the hydrocarbyl substituted acylating agent may be a terpolymer that is the reaction product of ethylene and at least one monomer that is an ethylenically unsaturated monomer having at least one tertiary nitrogen atom, with (i) an alkenyl ester of one or more aliphatic monocarboxylic acids having 1 to 24 carbon atoms or (ii) an alkyl ester of acrylic or methacrylic acid.

[0093] In an embodiment the nitrogen containing compound of the additional quaternary ammonium salts is an imidazole or nitrogen containing compound of either of formulas.



wherein R may be a C₁ to C₆ alkylene group; each of R₁ and R₂, individually, may be a C₁ to C₆ hydrocarbylene group; and each of R₃, R₄, R₅, and R₆, individually, may be a hydrogen or a C₁ to C₆ hydrocarbyl group. In one embodiment R₁ or R₂ can be, for example, a C₁, C₂ or C₃ alkylene group. In the same or different embodiments, each R₃, R₄, R₅, R₆ can be, for example, H or a C₁, C₂ or C₃ alkyl group.

[0094] In other embodiments, the quaternizing agent used to prepare the additional quaternary ammonium salts can be a dialkyl sulfate, an alkyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, a carboxylate, alkyl esters, or mixtures thereof. In some cases the quaternizing agent can be a hydrocarbyl epoxide. In some cases the quaternizing agent can be a hydrocarbyl epoxide in combination with an acid. In some cases the quaternizing agent can be a salicylate, oxalate or terephthalate. In an embodiment the hydrocarbyl epoxide is an alcohol functionalized epoxides or C₄ to C₁₄ epoxides.

[0095] In some embodiments, the quaternizing agent is multi-functional resulting in the additional quaternary ammonium salts being a coupled quaternary ammoniums salts.

[0096] Typical treat rates of additional detergents/dispersants to a fuel of the invention is 0 to 500 ppm, or 0 to 250 ppm, or 0 to 100 ppm, or 5 to 250 ppm, or 5 to 100 ppm, or 10 to 100 ppm.

[0097] In a particular embodiment, a fuel composition comprises the quaternary ammonium salts of the present invention and a cold flow improver. The cold flow improver is typically selected from (1) copolymers of a C₂- to C₄₀-olefin with at least one further ethylenically unsaturated monomer; (2) comb polymers; (3) polyoxyalkylenes; (4) polar nitrogen compounds; (5) sulfocarboxylic acids or sulfonic acids or derivatives thereof; and (6) poly(meth)acrylic esters. It is possible to use either mixtures of different representatives from one of the particular classes (1) to (6) or mixtures of representatives from different classes (1) to (6).

[0098] Suitable C₂- to C₄₀-olefin monomers for the copolymers of class (1) are, for example, those having 2 to 20 and especially 2 to 10 carbon atoms, and 1 to 3 and preferably 1 or 2 carbon-carbon double bonds, especially having one carbon-carbon double bond. In the latter case, the carbon-carbon double bond may be arranged either terminally (α -olefins) or internally. However, preference is given to α -olefins, more preferably α -olefins having 2 to 6 carbon atoms, for example propene, 1-butene, 1-pentene, 1-hexene and in particular ethylene. The at least one further ethylenically unsaturated monomer of class (1) is preferably selected from alkenyl carboxylates; for example, C₂- to C₁₄-alkenyl esters, for example the vinyl and propenyl esters, of carboxylic acids having 2 to 21 carbon atoms, whose hydrocarbon radical may be linear or branched among these, preference is given to the vinyl esters, examples of suitable alkenyl carboxylates are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl neopentanoate, vinyl hexanoate, vinyl neononanoate, vinyl neodecanoate and the corresponding propenyl esters, (meth)acrylic esters; for example, esters of (meth)acrylic acid with C₁- to C₂₀-alkanols, especially C₁- to C₁₀-alkanols, in particular with methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol and decanol, and structural isomers thereof and further olefins; preferably higher in molecular weight than the abovementioned C₂- to C₄₀-olefin base monomer for example, the olefin base monomer used is ethylene or propene, suitable further olefins are in particular C₁₀- to C₄₀- α -olefins.

[0099] Suitable copolymers of class (1) are also those which comprise two or more different alkenyl carboxylates in copolymerized form, which differ in the alkenyl function and/or in the carboxylic acid group. Likewise suitable are copolymers which, as well as the alkenyl carboxylate(s), comprise at least one olefin and/or at least one (meth)acrylic ester in copolymerized form.

[0100] Terpolymers of a C₂- to C₄₀- α -Olefin, a C₁- to C₂₀-alkyl ester of an ethylenically unsaturated monocarboxylic acid having 3 to 15 carbon atoms and a C₂- to C₁₄-alkenyl ester of a saturated monocarboxylic acid having 2 to 21 carbon atoms are also suitable as copolymers of class (K1). Terpolymers of this kind are described in WO 2005/054314. A typical terpolymer of this kind is formed from ethylene, 2-ethylhexyl acrylate and vinyl acetate.

[0101] The at least one or the further ethylenically unsaturated monomer(s) are copolymerized in the copolymers of class (1) in an amount of preferably 1 to 50% by weight, especially 10 to 45% by weight and in particular 20 to 40% by weight, based on the overall copolymer. The main proportion in terms of weight of the monomer units in the copolymers of class (1) therefore originates generally from the C₂ to C₄₀ base olefins. The copolymers of class (1) can have a number-average molecular weight M_n of 1000 to 20,000, or 1000 to 10,000, or 1000 to 8000.

[0102] Typical comb polymers of component (2) are, for example, obtainable by the copolymerization of maleic anhydride or fumaric acid with another ethylenically unsaturated monomer, for example with an α -olefin or an unsaturated ester, such as vinyl acetate, and subsequent esterification of the anhydride or acid function with an alcohol having at least 10 carbon atoms. Further suitable comb polymers are copolymers of α -olefins and esterified comonomers, for example esterified copolymers of styrene and maleic anhydride or esterified copolymers of styrene and fumaric acid. Suitable comb polymers may also be polyfumarates or polymaleates. Homo- and copolymers of vinyl ethers are also suitable comb polymers. Comb polymers suitable as components of class (2) are, for example, also those described in WO 2004/035715 and in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs. 8, pages 117 to 253 (1974). Mixtures of comb polymers are also suitable.

[0103] Polyoxyalkylenes suitable as components of class (3) are, for example, polyoxyalkylene esters, polyoxyalkylene ethers, mixed polyoxyalkylene ester/ethers and mixtures thereof. These polyoxyalkylene compounds preferably comprise at least one linear alkyl group, preferably at least two linear alkyl groups, each having 10 to 30 carbon atoms and a polyoxyalkylene group having a number-average molecular weight of up to 5000. Such polyoxyalkylene compounds are described, for example, in EP-A 061 895 and also in U.S. Pat. No. 4,491,455. Particular polyoxyalkylene compounds are based on polyethylene glycols and polypropylene glycols having a number-average molecular weight of 100 to 5000. Additionally suitable are polyoxyalkylene mono- and diesters of fatty acids having 10 to 30 carbon atoms, such as stearic acid or behenic acid.

[0104] Polar nitrogen compounds suitable as components of class (4) may be either ionic or nonionic and may have at least one substituent, or at least two substituents, in the form of a tertiary nitrogen atom of the general formula $>NR^7$ in which R^7 is a C_8 - to C_{40} -hydrocarbon radical. The nitrogen substituents may also be quaternized i.e. be in cationic form. An example of such nitrogen compounds is that of ammonium salts and/or amides which are obtainable by the reaction of at least one amine substituted by at least one hydrocarbon radical with a carboxylic acid having 1 to 4 carboxyl groups or with a suitable derivative thereof. The amines may comprise at least one linear C_8 - to C_{40} -alkyl radical. Primary amines suitable for preparing the polar nitrogen compounds mentioned are, for example, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tetradecylamine and the higher linear homologs. Secondary amines suitable for this purpose are, for example, dioctadecylamine and methylbehnylamine. Also suitable for this purpose are amine mixtures, in particular amine mixtures obtainable on the industrial scale, such as fatty amines or hydrogenated tallamines, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, "Amines, aliphatic" chapter. Acids suitable for the reaction are, for example, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalene dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and succinic acids substituted by long-chain hydrocarbon radicals.

[0105] Sulfocarboxylic acids, sulfonic acids or derivatives thereof which are suitable as cold flow improvers of class (5) are, for example, the oil-soluble carboxamides and carboxylic esters of ortho-sulfobenzoic acid, in which the sulfonic acid function is present as a sulfonate with alkyl-substituted ammonium cations, as described in EP-A 261 957.

[0106] Poly(meth)acrylic esters suitable as cold flow improvers of class (6) are either homo- or copolymers of acrylic and methacrylic esters. Preference is given to copolymers of at least two different (meth)acrylic esters which differ with regard to the esterified alcohol. The copolymer optionally comprises another different olefinically unsaturated monomer in copolymerized form. The weight-average molecular weight of the polymer can be 50,000 to 500,000. The polymer may be a copolymer of methacrylic acid and methacrylic esters of saturated C_{14} and C_{15} alcohols, the acid groups having been neutralized with hydrogenated tallamine. Suitable poly(meth)acrylic esters are described, for example, in WO 00/44857.

[0107] The cold flow improver or the mixture of different cold flow improvers is added to the middle distillate fuel or diesel fuel in a total amount of preferably 0 to 5000 ppm by weight, or 10 to 5000 ppm by weight, or 20 to 2000 ppm by weight, or 50 to 1000 ppm by weight or 100 to 700 ppm by weight, for example of 200 to 500 ppm by weight.

Industrial Application

[0108] In one embodiment the invention is useful in a liquid fuel in an internal combustion engine. The internal combustion engine may be a gasoline or diesel engine. Exemplary internal combustion engines include, but are not limited to, spark ignition and compression ignition engines; 2-stroke or 4-stroke cycles; liquid fuel supplied via direct injection, indirect injection, port injection and carburetor; common rail and unit injector systems; light (e.g. passenger car) and heavy duty (e.g. commercial truck) engines; and engines fuelled with hydrocarbon and non-hydrocarbon fuels and mixtures thereof. The engines may be part of integrated emissions systems incorporating such elements as; EGR systems; aftertreatment including three-way catalyst, oxidation catalyst, NO_x absorbers and catalysts, catalyzed and non-catalyzed particulate traps optionally employing fuel-borne catalyst; variable valve timing; and injection timing and rate shaping.

[0109] In one embodiment, the technology may be used with diesel engines having direct fuel injection systems wherein the fuel is injected directly into the engine's combustion chamber. The ignition pressures may be greater than 1000 bar

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

[0110] In a further embodiment, the imide quat technology is useful for providing at least equivalent, if not improved detergency (deposit reduction and/or prevention) performance in both the traditional and modern diesel engine compared to a 1000 M_n quaternary ammonium compound. In addition, the technology can provide improved water shedding (or demulsifying) performance compared to 1000 M_n quaternary ammonium compounds in both the traditional and modern diesel engine. In yet another embodiment, the disclosed technology may be used to improve the cold temperature operability or performance of a diesel fuel (as measured by the ARAL test).

[0111] Embodiments of the present technology may provide at least one of antiwear performance, friction modification (particularly for enhancing fuel economy), detergent performance (particularly deposit control or varnish control), dispersancy (particularly soot control, or sludge control), or corrosion control.

Deposit Control

[0112] As fuel burns inside an engine, solid carbonaceous by-products may be produced. The solid by-products may stick to the interior walls of the engine and are often referred to as deposits. If left unchecked, engines fouled by deposits may experience a loss in engine power, fuel efficiency, or drivability.

[0113] In traditional diesel engines operating at low pressures (i.e., <35 MPa), deposits form on the fuel injector tips and in the spray holes. These injector tip deposits can disrupt the spray pattern of the fuel, potentially causing a reduction in power and fuel economy. Deposits may also form inside the injectors in addition to forming on the tips. These internal deposits are commonly called internal diesel injector deposits (IDIDs). It is believed that IDIDs have a minor impact, if any on the operation of traditional diesel engines operating at low pressures.

[0114] With the introduction of diesel engines equipped with high pressure common rail fuel injector systems (i.e., >35MPa), however, IDIDs may be more problematic than in traditional diesel engines. In high pressure common rail fuel injector systems, IDIDs can form on injector moving parts, such as the needle and command piston or control valve. IDIDs can hinder the movement of the injector parts, impairing the injection timing and the quantity of fuel injected. Since modern diesel engines operate on precise multiple injection strategies in order to maximize efficiency and performance of combustion, IDIDs can have a serious adverse effect on engine operation and vehicle drivability.

[0115] High pressure common rail fuel injector systems are both more susceptible and more prone to IDID formation. These advanced systems have tighter tolerances due to their extremely high operating pressures. Likewise, in some cases the clearance between moving parts in the injectors is only a few microns or less. As such, advanced diesel fuel systems are more susceptible to IDIDs. Deposits may be likely to form in these systems because of their higher operating temperatures which can oxidize and decompose the chemically unstable components of the diesel fuel. Another factor that may also contribute to IDID issues in high pressure common rail systems is that these injectors often have lower activation forces making them even more prone to sticking than in high pressure systems. The lower activation forces may also cause some of the fuel to "leak back" into the injectors, which may also contribute to IDID.

[0116] Without limiting this specification to one theory of operation, it is believed that IDIDs are formed from when the hydrophilic-lipophilic balance (HLB) of sparingly soluble contaminants moves to a level where the hydrophilic head group dominates over the lipophilic tail. As the length of the lipophilic tail decreases, the hydrophilic head group begins to dominate. The structure of the tail (branched versus linear) and/or may also affect the solubility of the contaminants. In addition, as the polarity of the head group sparingly soluble contaminants increase, its solubility decreases. While there may be multiple causes and sources of IDID, two types of IDIDs have been identified; 1) metal (sodium) carboxylate-type IDIDs, often referred to as "metal soaps" or "sodium soaps", and 2) amide-type IDIDs, often referred to as "amide lacquers".

[0117] Advanced chemical analysis techniques have been used to obtain more detailed structural information on IDIDs to help identify the sources of the problem. Detailed analysis of metal soap-type IDIDs has helped identify corrosion inhibitors, such as alkenyl succinic acids, as culprits in IDID formation. The corrosion inhibitors, for example, dodecenyl succinic acid (DDSA) and hexadecenyl succinic acid (HDSA) (two commonly used pipeline corrosion inhibitors in the petroleum industry), pick up trace levels of sodium and other metals in the fuel left over from the refinery process. Tests have been conducted using engines compliant with US Tier 3 emission standards to explore the underlying structure activity relationships of sodium soap formation. Without limiting this specification to one theory of operation, it is believed that the formation of metal soap IDIDs is dependent upon the size (number of carbons) of the hydrocarbon tail of the

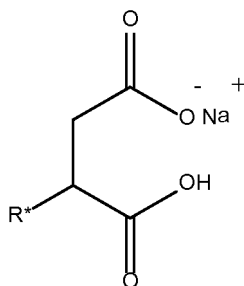
"soap" and the number of carboxylic acids groups (CO₂H) in the head group of the corrosion inhibitor. It was observed that the tendency to form deposits increases when the inhibitor had a short tail and multiple carboxylic acids in the head group. In other words, dicarboxylic acid corrosion inhibitors with a lower number average molecular weight (M_n) ranging between 280 and 340, have a greater tendency to form sodium soap deposits than corrosion inhibitors with a higher number average molecular weight. Persons of ordinary skill in the art will understand that there may be some low molecular weight polymers present in corrosion inhibitors with a number average molecular weight above 340.

[0118] These laboratory tests have also shown that deposits can form with as little as 0.5 to 1 ppm of sodium in the fuel along with 8 to 12 ppm of a corrosion inhibitor, such as DDSA or HDSA, and it is possible that real world concentrations may be lower with deposits occurring over longer periods of time, such as 0.01 to 0.5 ppm metal with 1 to 8 ppm corrosion inhibitor.

[0119] These metal soaps can be referred to as low molecular weight soaps, and can be represented, for example, by structures of:



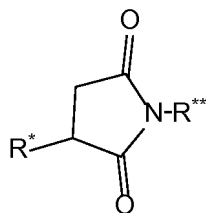
wherein R^* is a linear, branched or cyclic hydrocarbyl group having 10 to 36 carbon atoms, or 12 to 18, or 12 to 16 carbon atoms, M^+ is a metal contaminant, such as sodium, calcium, or potassium, and x is an integer from 1 to 4, 2 to 3, or 2. One class of low molecular weight soaps are those represented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



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

[0120] Amide lacquer formation is less certain but it has been suggested that it is derived from polyisobutylene succinimides (PIBSIs) with low number average molecular weight (M_n) which are added to diesel fuel to control nozzle fouling. Low molecular weight PIBSIs may have an average M_n of 400 or less using gel permeation chromatography (GPC) and a polystyrene calibration curve. Alternatively, low M_n PIBSIs may have an average M_n of 200 to 300. These low molecular weight PIBSIs may be byproducts formed from low molecular weight PIBS present in the production process. While generally higher molecular weight polyisobutylene (PIB) with an average M_n of 1000 is used to generate the PIBSIs, low molecular weight PIBs may be present as contaminants. Low molecular weight PIBSIs may also form when increasing the reaction temperature to remove excess reactants or catalysts. Again, while completely eliminating low M_n PIBSIs from anti-foulants might result in reducing IDID formation, complete elimination might not be practical. Accordingly, low M_n PIBSIs may be present in an amount of 5 wt% or less of a total weight of the PIBIs used. It is hypothesized, without limiting this specification to one theory of operation, that the low molecular weight portion of the PIBSI is responsible for deposit formation as it is only sparingly soluble in diesel and thus deposits on the injector surface. In fact, amide lacquer IDIDs have been shown to be linked to low molecular weight species by demonstrating that amide lacquer IDIDs can be produced in US Tier 3-compliant engines using a low molecular weight PIBSI fraction. Here again, laboratory tests have shown that as little as 5 ppm of the low molecular weight PIBSI can cause deposit issues and it is possible that real world concentrations may be lower with deposits occurring over longer periods of time, such as from 0.01 to 5 ppm low molecular weight PIBSI.

[0121] Such low molecular weight PIBSI fractions can be represented, for example, by structure:



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

[0122] The degree of bismaleation of the low molecular weight PIBSI may also affect the polarity of the head group, thereby reducing the PIBSI's solubility in the fuel.

[0123] Another factor that may contribute to IDID formation is the change in diesel fuel to sulfur-free diesel fuel. Sulfur-free diesel fuel is produced by hydrotreating wherein polyaromatics are reduced, thereby lowering the boiling point of the final fuel. As the final fuel is less aromatic, it is also less polar and therefore less able to solubilize sparingly soluble contaminants such as metal soaps or amide lacquers.

[0124] The formation of IDIDs can be reduced in a fuel containing low molecular weight soaps or low molecular weight PIBSI fractions by adding to the fuel the imide quats with a number average molecular weight ranging from 1300 to 3000 described herein. Thus, an embodiment of the present technology includes fuel compositions comprising at least one low molecular weight soap and the imide quat as described above.

[0125] In another embodiment, a method of reducing and/or preventing internal diesel injector deposits is disclosed. The method may comprise employing a fuel composition comprising the imide quat as described above. The fuel may have a low molecular weight soap present therein. In an embodiment, the low molecular weight soap can be derived from the presence of from 0.01 to 5 ppm of a metal and 1 to 12, or 1 to 8, or 8 to 12 ppm of a corrosion inhibitor. Exemplary metals include, but are not limited to, sodium, calcium, and potassium. The corrosion inhibitors may comprise an alkenyl succinic acid such as dodecenyl succinic acid (DDSA) or hexadecenyl succinic acid (HDSA). In yet another embodiment of the present technology the fuel composition may have a low molecular weight polyisobutylene succinimides (PIBSI) present therein. The low molecular weight PIBSI may be present in the fuel at greater than 0.01 ppm, such as, for example, 5 to 25 ppm, or from 0.01 to 5 ppm of a low molecular weight PIBSI.

[0126] In a further embodiment, the technology may include a method of cleaning-up deposits in a diesel engine, such as, a diesel engine having a high pressure (i.e., above 35MPa) common rail injector system, by operating the engine with a fuel containing an imide quat therein. In an embodiment, the clean-up method includes reducing and/or preventing IDID causing deposits derived from the presence of a low molecular weight soap. In an embodiment, the clean-up method includes reducing and/or preventing IDID causing deposits derived from the presence of a low molecular weight PIBSI.

[0127] 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.

[0128] 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 in its intended use, may not be susceptible of easy description.

EXAMPLES

[0129] The invention will be further illustrated by the following examples, which sets forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

Example 1 - Formation of 1000 M_n Polyisobutylene Succinic Anhydride (PIBSA)

[0130] A 1000 number average molecular weight (M_n) polyisobutylene (PIB) (2000 g., 2.0 moles, high-vinylidene PIB) having greater than 70 % vinylidene groups is charged to a 5-liter flange flask equipped with overhead stirrer, air condenser, nitrogen inlet, thermocouple and Eurotherm™ temperature controller (reaction kit).

[0131] Maleic anhydride (245 g, 2.5 moles) is then charged to the reaction vessel. The batch is agitated under a nitrogen blanket and slowly heated to 203 °C over a 90 minute period. The batch is maintained at 203°C for 24 hours.

[0132] The reaction kit is then reconfigured for vacuum stripping. The batch is stripped at 203 °C and 0.05 bar to remove unreacted maleic anhydride. The batch comprising the formed PIBSA is then cooled back to 50 °C and decanted

into a storage vessel.

Example 2 - Formation of Quaternizable Compound - 1000 M_n PIBSA and Dimethylaminopropylamine (DMAPA)

- 5 **[0133]** A 1000 M_n PIBSA (1950.3g, 1.86 moles) product of Example 1 is charged to a 3-liter flask equipped with a water condenser and Dean Stark trap, a thermocouple, a dropping funnel, an overhead stirrer and Nitrogen inlet and heated to 90 °C.
- [0134]** Dimethylaminopropylamine (189.7g, 1.86 moles) DMAPA is added to the flask via the dropping funnel over 50 minutes. The batch temperature is kept below 120 °C while adding the DMAPA.
- 10 **[0135]** Once all the DMAPA is added, the reaction is slowly heated to 150 °C and maintained at that temperature for 3 hours. Approximately 40 g of water is collected in the Dean Stark apparatus while heating. The remaining product is the 1000 M_n PIBSA/DMAPA quaternizable compound.

15 Comparative Example 3 - Formation of a 1000 M_n PIBSA/DMAPA Quaternary Ammonium Salt using Propylene Oxide (an imide/propylene oxide quat)

- [0136]** A 1000 M_n PIBSA/DMAPA quaternizable compound (551.1g, 0.54 moles, as prepared in Example 2) is added to a 1-liter flask equipped with a water condenser, a thermocouple, a syringe pump, an overhead stirrer and nitrogen inlet.
- 20 **[0137]** 2-ethylhexanol (124.5g, 0.96 moles), acetic acid (32.4g, 0.54 moles) and water (5.0g, 0.287 moles) are also charged to the 1-liter flask. The batch is then heated to 75 °C, under agitation and nitrogen atmosphere. Propylene oxide is added via a syringe pump over 4 hours. The batch is then held for 4 hours at 75 °C before being cooled back to 50 °C. The imide/propylene oxide quat is then decanted into a storage vessel.

25 Comparative Example 4 - Formation of a 1000 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxybutane (an imide/epoxybutane quat)

- [0138]** A 1000 M_n PIBSA/DMAPA quaternizable compound (476.2, 0.47 moles, as prepared in Example 2) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, a syringe pump, an overhead stirrer and a nitrogen inlet.
- 30 **[0139]** 2-ethylhexanol (136.6 g, 1.05 moles), acetic acid (28.24 g, 0.47 moles) and water (4.76 g, 0.264 moles) are also charged to the 1-liter flask. The batch is then heated to 90 °C, under agitation and nitrogen atmosphere. 1,2-epoxybutane (37.3g, 0.51moles) is added via the syringe pump over 2 hours. The batch is then held for 3 hours at 90 °C before being cooled back to 50 °C. The imide/epoxybutane quat is then decanted into a storage vessel.

35 Example 5 - Formation of a 1000 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxydodecane (an imide/epoxydodecane quat) (for reference)

- [0140]** A 1000 M_n PIBSA/DMAPA quaternizable compound (791.4 g, 0.776 moles, as prepared in Example 2) is added to a 2-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.
- 40 **[0141]** 2-ethylhexanol (315.4 g, 2.43 moles), 1,2-epoxydodecane (146 g, 0.793 moles), acetic acid (46 g, 0.77 moles), and water are also charged to the 2-liter flask. Agitation is then initiated (200 rpm) and a slow nitrogen purge is introduced. The batch is then heated to 75 °C and maintained at temperature for 4 hours. The imide/epoxydodecane quat is then then cooled before it is transferred into a storage vessel.

45 Example 6 - Formation of a 1000 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxyhexadecane (an imide/epoxyhexadecane quat) (for reference)

- [0142]** A 1000 M_n PIBSA/DMAPA quaternizable compound (500 g, 0.495 moles, as prepared in Example 2) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.
- 50 **[0143]** 2-ethylhexanol (163.34 g, 1.26 moles) and water (5 g, 0.27 moles) are added to the flask and heated to 90 °C. Acetic acid (29.65, 0.494 moles) and 1,2-epoxyhexadecane (118.71 g, 0.494 moles) are added to the flask. Agitation is then initiated (200 rpm) and a slow nitrogen purge is introduced. The batch is held at 90 °C for 3 hours. The imide/epoxyhexadecane quat is then then cooled before it is transferred into a storage vessel.

55 Example 7 - Formation of a 1000 M_n PIBSA/DMAPA Quaternary Ammonium Salt using Glycidol (an imide/glycidol quat)

- [0144]** A 1000 M_n PIBSA/DMAPA quaternizable compound (845 g, 0.78 moles, as prepared in Example 2) is added to a 2-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0145] 2-ethylhexanol (315.4 g, 2.43 moles), glycidol (63 g, 0.85 moles), acetic acid (47.3 g, 0.78 moles), and water (8.2 g, 0.45 moles) are also charged to the 2-liter flask. Agitation is then initiated (200 rpm) and a slow nitrogen purge is introduced. The batch is then heated to 75 °C and maintained at temperature for 4 hours. The imide/glycidol quat is then then cooled before it is transferred into a storage vessel.

Example 8 - Formation of 550 M_n Polyisobutylene Succinic Anhydride (PIBSA)

[0146] A 550 number average molecular weight (M_n) polyisobutylene (PIB) (2840 g, 5.163 moles, mid-vinylidene PIB available from Daelim) having greater than 20 % vinylidene groups is charged to a 5-liter flange flask equipped with overhead stirrer, air condenser, nitrogen inlet, thermocouple and Eurotherm™ temperature controller (reaction kit).

[0147] Maleic anhydride (632.2 g 6.449 moles) is then charged to the reaction vessel. The batch is agitated under a nitrogen blanket and slowly heated to 203 °C over a 90 minute period. The batch is maintained at 203°C for 24 hours.

[0148] The reaction kit is then reconfigured for vacuum stripping. The batch is stripped at 203 °C and 0.05 bar to remove unreacted maleic anhydride. The batch comprising the formed PIBSA and ~ 20% unreacted polyisobutylene is then cooled back to 50 °C and decanted into a storage vessel.

Example 9 - Formation of Quaternizable Compound - 550 M_n PIBSA and Dimethylaminopropylamine (DMAPA)

[0149] The 550 M_n PIBSA (1556.2 g, 2.29 moles) (product of Example 8) is charged to a 3-liter flask equipped with a water condenser and Dean Stark trap, a thermocouple, a dropping funnel, an overhead stirrer and Nitrogen inlet and heated to 90 °C.

[0150] DMAPA (233.4 g, 2.29moles) is added to the flask via the dropping funnel over 50 minutes. The batch temperature is kept below 120 °C while adding the DMAPA.

[0151] Once all the DMAPA is added, the reaction is slowly heated to 150 °C and maintained at that temperature for 3 hours. Approximately 40g of water is collected in the Dean Stark apparatus while heating. The remaining product is the 550 M_n PIBSA/DMAPA quaternizable compound.

Example 10 (prophetic) - Formation of a 550 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxybutane (an imide/epoxybutane quat) (for reference)

[0152] The 550 M_n PIBSA/DMAPA quaternizable compound of Example 9 (475 g, 0.62 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, a syringe pump, an overhead stirrer and a nitrogen inlet.

[0153] 2-ethylhexanol (136 g, 1.05 moles), acetic acid (37.3 g, 0.62 moles) and water (4.4g, 0.24 moles) are also charged to the 1-liter flask. The batch is then heated to 75 °C, under agitation and nitrogen atmosphere. 1,2-epoxybutane (48.9 g, 0.68 moles) is added via the syringe pump over 2 hours. The batch is then held for 3 hours at 75 °C. The imide/epoxybutane quat is then cooled and discharged into a storage vessel.

Example 11 (prophetic) - Formation of a 550 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxydodecane (an imide/epoxydodecane quat) (for reference)

[0154] The 550 M_n PIBSA/DMAPA quaternizable compound of Example 9 (470 g, 0.61 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0155] 2-ethylhexanol (136 g, 1.05 moles), 1,2-epoxydodecane (114.1 g, 0.62 moles), acetic acid (37 g, 0.62 moles), and water (4.4 g, 0.24 moles) are also charged to the 1-liter flask. The batch is then heated to 75 °C under agitation and nitrogen and maintained at temperature for 3 hours. The imide/epoxydodecane quat is then then cooled before it is transferred into a storage vessel.

Example 12 (prophetic) - Formation of a 550 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxyhexadecane (an imide/epoxyhexadecane quat) (for reference)

[0156] The 550 M_n PIBSA/DMAPA quaternizable compound of Example 9 (470 g, 0.61 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0157] 2-ethylhexanol (136 g, 1.05 moles), 1,2-epoxyhexadecane (148.99 g, 0.62 moles), acetic acid (37.0 g, 0.62 moles), and water (4.4 g, 0.24 moles) are added to the flask and heated to 75 °C while agitating under nitrogen. The batch is held at 75 °C for 3 hours. The imide/epoxyhexadecane quat is then then cooled before it is transferred into a storage vessel.

Example 13 (prophetic) - Formation of a 550 M_n PIBSA/DMAPA Quaternary Ammonium Salt using Glycidol (an imide/glycidol quat)

[0158] The 550 M_n PIBSA/DMAPA quaternizable compound of Example 9 (471 g, 0.62 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0159] 2-ethylhexanol (138.0 g, 1.06 moles), glycidol (48.2 g, 0.65 moles), acetic acid (37.2 g, 0.62 moles), and water (4.1 g, 0.22 moles) are also charged to the 1-liter flask. Agitation is then initiated (200 rpm) and a slow nitrogen purge is introduced. The batch is then heated to 75 °C and maintained at temperature for 4 hours. The imide/glycidol quat is then then cooled before it is transferred into a storage vessel.

Example 14 (prophetic) - Formation of 2300 M_n Polyisobutylene Succinic Anhydride (PIBSA)

[0160] A 2300 number average molecular weight (M_n) polyisobutylene (PIB) (2000 g., 0.87 moles) high-vinylidene PIB having greater than 20 % vinylidene groups is charged to a 5-liter flange flask equipped with overhead stirrer, air condenser, nitrogen inlet, thermocouple and Eurotherm™ temperature controller (reaction kit).

[0161] Maleic anhydride (165.5 g, 1.70 moles) is then charged to the reaction vessel. The batch is agitated under a nitrogen blanket and slowly heated to 203 °C over a 90 minute period. The batch is maintained at 203 °C for 24 hours.

[0162] The reaction kit is then reconfigured for vacuum stripping. The batch is stripped at 203 °C and 0.05 bar to remove unreacted maleic anhydride. Diluent oil, such as mineral oil (1116.8 g), is added to the batch. The batch comprising the formed PIBSA is then cooled back to 50 °C and decanted into a storage vessel.

Example 15 - Formation of Quaternizable Compound - 2300 M_n PIBSA and Dimethylaminopropylamine (DMAPA)

[0163] A 2300 M_n PIBSA (3000 g, 1.52 moles, as prepared in Example 14) is charged to a 5-liter flask equipped with a water condenser and Dean Stark trap, a thermocouple, a dropping funnel, an overhead stirrer and Nitrogen inlet and heated to 90 °C.

[0164] DMAPA (154.72 g, 1.517 moles) is added to the flask via the dropping funnel over 40 minutes. An exotherm increasing 6 °C was observed. Once all the DMAPA is added, the reaction is slowly heated to 150 °C and maintained at that temperature for 3 hours, and approximately 25g water is collected in Dean Stark trap. The resulting product is a 2300 M_n PIBSA/DMAPA quaternizable compound.

Example 16 (prophetic) - Formation of a 2300 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxydodecane (an imide/epoxydodecane quat) (for reference)

[0165] The 2300 M_n PIBSA/DMAPA quaternizable compound of Example 15 (550.8 g, 0.29 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0166] 2-ethylhexanol (145.4 g, 1.12 moles), 1,2-epoxydodecane (51.55 g, 0.28 moles), acetic acid (17.4 g, 0.29 moles), and water (5.6 g, 0.31 moles) are also charged to the 1-liter flask. The batch is then heated to 75 °C under agitation and nitrogen and maintained at temperature for 3 hours and 15 minutes. The imide/epoxydodecane quat is then then cooled before it is transferred into a storage vessel.

Example 17 - Formation of a 2300 M_n PIBSA/DMAPA Quaternary Ammonium Salt using 1,2-Epoxyhexadecane (an imide/epoxyhexadecane quat) (for reference)

[0167] The 2300 M_n PIBSA/DMAPA quaternizable compound of Example 15 (550.8 g, 0.29 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0168] 2-ethylhexanol (145.4 g, 1.12 moles), 1,2-epoxyhexadecane (67.4 g, 0.28 moles), acetic acid (17.4 g, 0.29 moles), and water (5.6 g, 0.31 moles) are added to the flask and heated to 75 °C while agitating under nitrogen. The batch is held at 75 °C for 3 hours and 15 minutes. The imide/epoxyhexadecane quat is then then cooled before it is transferred into a storage vessel.

Example 18 - Formation of a 2300 M_n PIBSA/DMAPA Quaternary Ammonium Salt using Glycidol (an imide/glycidol quat)

[0169] The 2300 M_n PIBSA/DMAPA quaternizable compound of Example 15 (550 g, 0.25 moles) is added to a 1-liter flask flange flask equipped with a water condenser, a thermocouple, an overhead stirrer and a nitrogen inlet.

[0170] 2-ethylhexanol (175.6 g, 1.35 moles), glycidol (18.85 g, 0.25 moles), acetic acid (15.28 g, 0.25 moles), and water (5 g, 0.27 moles) are also charged to the 1-liter flask. Agitation is then initiated (200 rpm) and a slow nitrogen purge is introduced. The batch is then heated to 90 °C and maintained at temperature for 3 hours. The imide/glycidol

quat is then then cooled before it is transferred into a storage vessel.

Demulsification (Water Shedding) Testing

[0171] The demulsification test is performed to measure the epoxide quats' ability to demulsify fuel and water mixtures as compared to the 1000 M_n imide/propylene oxide quat of Comparative Example 3. The demulsification test is run according to the procedure in ASTM D1094-07 ("Standard Test Method for Water Reaction of Aviation Fuels"). The quaternary ammonium salt is added to room temperature fuel at 60 ppm actives by weight based on a total weight of the fuel. A commercially available demulsifier (Tolad 9327 available from Baker Hughes) is added to the fuel at 18 ppm by weight based on a total weight of the fuel.

[0172] The fuel (80 mL) is then added to a clean, 100 mL-graduated cylinder. A phosphate buffer solution with a pH of 7.0 (20 mL) is then added to the graduated cylinder and the cylinder is stoppered. The cylinder is shaken for 2 minutes at 2 to 3 strokes per second and placed on a flat surface. The volume of the aqueous layer, or water recovery, is then measured at 3, 5, 7, 10, 15, 20, and 30-minute intervals.

[0173] The results of the demulsification tests are shown in Table 1 below and in FIG. 1.

Table 1

	3	5	7	10	15	30	Time
Example 4	2.5	8.5	14	18	19	20	Water recovered (mL)
Example 6	11	18	19	20	20	20	Water recovered (mL)
Example 17	2.5	8.5	14	18	19	20	Water recovered (mL)
Example 5	10.5	18	19	20	20	20	Water recovered (mL)
Example 7	0	0	0	2	15	20	Water recovered (mL)
Example 18	7	8	13	15	17	19	Water recovered (mL)
Comparative Example 3	2	2	4	4	5	10	Water recovered (mL)

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

[0174] Deposit tests are performed using Peugeot S.A.'s XUD 9 engine in accordance with the procedure in CEC F-23-01. For the first deposit test, air flow is measured through clean injector nozzles of the XUD 9 engine using an air-flow rig. The engine is then run on a reference fuel (RF79) and cycled through various loads and speeds for a period of 10 hours to simulate driving and allow any formed deposits to accumulate. The air-flow through the nozzles are measured again using the air-flow rig. The percentage of air flow loss (or flow remaining) is then calculated.

[0175] A set of deposit tests are performed using the same steps above, except 10 ppm actives of the epoxide quat are added to the reference fuel. A second set of deposit tests are performed using the same steps above, except 30 ppm actives are added to the reference fuel.

[0176] The results of the deposit tests for the first and second sets are shown in Table 2 and FIG. 2 and in Table 3 and FIG. 3 respectively.

Table 2 - 10 ppm Actives

	Flow Loss (%)	Flow Remaining (%)
Example 4	65.5	34.5
Example 5	72.1	27.9
Example 7	70.5	29.5
Reference Fuel	80	20

Table 3 - 30 ppm Actives

	Flow Loss (%)	Flow Remaining (%)
Example 4	25.9	74.1

(continued)

	Flow Loss (%)	Flow Remaining (%)
Example 6	13.0	87.0
Example 7	8.6	91.4
Example 18	19.0	81.0
Reference Fuel	80	20

[0177] 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.

[0178] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

[0179] In this regard, the scope of the invention is to be limited only by the following claims.

Claims

1. Use of an epoxide quaternary ammonium salt ("epoxide quat") for improving the water shedding performance of a fuel composition, wherein the epoxide quat comprises the reaction product of:
 - a) a quaternizable compound that is the reaction product of:
 - (i) a hydrocarbyl-substituted acylating agent, wherein the hydrocarbyl-substituent has a number average molecular weight ranging from 100 to 5000, and comprises at least one polyisobutenyl succinic anhydride or polyisobutenyl succinic acid, and
 - (ii) a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with said hydrocarbyl-substituted acylating agent, and further having at least one quaternizable amino group; and
 - b) a quaternizing agent comprising alcohol functionalized epoxides, preferably wherein the quaternizing agent is glycidol.
2. The use of claim 1, wherein the hydrocarbyl-substituent of said acylating agent has a number average molecular weight of 550.
3. The use of any of previous claim, wherein the quaternizable amino group is a primary, secondary or tertiary amino group.
4. The use of any previous claim wherein the quaternizing agent is employed in the presence of a protic solvent, preferably wherein the protic solvent comprises 2-ethylhexanol, water, and mixtures thereof.
5. The use of any previous claim wherein the quaternizing agent is employed in the presence of an acid, preferably wherein the acid is present in the structure of the acylating agent.
6. The use of any previous claim further comprising at least one other additive, preferably wherein the at least one other additive comprises a detergent, a dispersant, a demulsifier, a lubricity agent, a cold flow improver, an antioxidant, or a mixture thereof.

7. The use of claim 6, wherein the at least one other additive comprises at least one hydrocarbyl-substituted succinic acid or at least one hydrocarbyl-substituted quaternary ammonium salt.
8. The use of any previous claim wherein the fuel is liquid at room temperature, preferably wherein the fuel is gasoline or diesel.

Patentansprüche

1. Verwendung eines epoxidhaltigen quaternären Ammoniumsalzes ("Epoxidquat") zur Verbesserung des Wasserabscheidevermögens einer Kraftstoffzusammensetzung, wobei das Epoxidquat das Reaktionsprodukt von:

a) einer quaternisierten Verbindung, bei der es sich um das Reaktionsprodukt:

- (i) eines hydrocarbylsubstituierten Acylierungsmittels, wobei der Hydrocarbyl-substituent ein zahlenmittleres Molekulargewicht im Bereich von 100 bis 5000 aufweist und mindestens ein Polyisobutenylbernsteinsäureanhydrid oder mindestens eine Polyisobutenylbernsteinsäure umfasst, und
- (ii) einer stickstoffhaltigen Verbindung mit einem Sauerstoff- oder Stickstoffatom, das mit dem hydrocarbylsubstituierten Acylierungsmittel reagieren kann, und ferner mit mindestens einer quaternisierbaren Aminogruppe

handelt; und

b) einem Quaternisierungsmittel, das alkoholfunktionalisierte Epoxide umfasst, wobei es sich bei dem Quaternisierungsmittel vorzugsweise um Glycidol handelt;

umfasst.

2. Verwendung nach Anspruch 1, wobei der Hydrocarbyl-substituent des Acylierungsmittels ein zahlenmittleres Molekulargewicht von 550 aufweist.
3. Verwendung nach einem der vorhergehenden Ansprüche, wobei es sich bei der quaternisierbaren Aminogruppe um eine primäre, sekundäre oder tertiäre Aminogruppe handelt.
4. Verwendung nach einem der vorhergehenden Ansprüche, wobei das Quaternisierungsmittel in Gegenwart eines protischen Lösungsmittels eingesetzt wird, wobei das protische Lösungsmittel vorzugsweise 2-Ethylhexanol, Wasser und Mischungen davon umfasst.
5. Verwendung nach einem der vorhergehenden Ansprüche, wobei das Quaternisierungsmittel in Gegenwart einer Säure eingesetzt wird, wobei die Säure vorzugsweise in der Struktur des Acylierungsmittels vorliegt.
6. Verwendung nach einem der vorhergehenden Ansprüche, ferner umfassend mindestens ein anderes Additiv, wobei es sich bei dem mindestens einen anderen Additiv vorzugsweise um ein Detergens, ein Dispergiermittel, einen Demulgator, ein Schmiermittel, einen Kaltfließverbesserer, ein Antioxidans oder eine Mischung davon handelt.
7. Verwendung nach Anspruch 6, wobei das mindestens eine andere Additiv mindestens eine hydrocarbylsubstituierte Bernsteinsäure oder mindestens ein hydrocarbylsubstituiertes quaternäres Ammoniumsalz umfasst.
8. Verwendung nach einem der vorhergehenden Ansprüche, wobei der Kraftstoff bei Raumtemperatur flüssig ist, wobei es sich bei dem Kraftstoff vorzugsweise um Benzin oder Diesel handelt.

Revendications

1. Utilisation d'un sel d'ammonium quaternaire époxydé (« quat époxydé ») pour améliorer les performances de perte d'eau d'une composition de carburant, le quat époxydé comprenant le produit de réaction de :

a) un composé quaternisable qui est le produit de réaction de :

(i) un agent acylant à substitution hydrocarbyle, le substituant hydrocarbyle ayant un poids moléculaire moyen en nombre allant de 100 à 5000, et comprenant au moins un anhydride polyisobuténylsuccinique ou acide polyisobuténylsuccinique, et

(ii) un composé contenant de l'azote ayant un atome d'oxygène ou d'azote susceptible de réagir avec ledit agent acylant à substitution hydrocarbyle, et ayant en outre au moins un groupe amino quaternisable ; et

b) un agent de quaternisation comprenant des époxydes fonctionnalisés par alcool, l'agent de quaternisation étant de préférence le glycidol.

2. Utilisation de la revendication 1, dans laquelle le substituant hydrocarbyle dudit agent acylant a un poids moléculaire moyen en nombre de 550.

3. Utilisation d'une quelconque revendication précédente, dans laquelle le groupe amino quaternisable est un groupe amino primaire, secondaire ou tertiaire.

4. Utilisation d'une quelconque revendication précédente dans laquelle l'agent de quaternisation est employé en présence d'un solvant protique, le solvant protique comprenant de préférence du 2-éthylhexanol, de l'eau, et des mélanges de ceux-ci.

5. Utilisation d'une quelconque revendication précédente dans laquelle l'agent de quaternisation est employé en présence d'un acide, l'acide étant de préférence présent dans la structure de l'agent acylant.

6. Utilisation d'une quelconque revendication précédente comprenant en outre au moins un autre additif, l'au moins un autre additif comprenant de préférence un détergent, un dispersant, un désémulsifiant, un agent d'onctuosité, un agent améliorant l'écoulement à froid, un antioxydant, ou un mélange de ceux-ci.

7. Utilisation de la revendication 6, dans laquelle l'au moins un autre additif comprend au moins un acide succinique à substitution hydrocarbyle ou au moins un sel d'ammonium quaternaire à substitution hydrocarbyle.

8. Utilisation d'une quelconque revendication précédente dans laquelle le carburant est liquide à température ambiante, le carburant étant de préférence de l'essence ou du diesel.

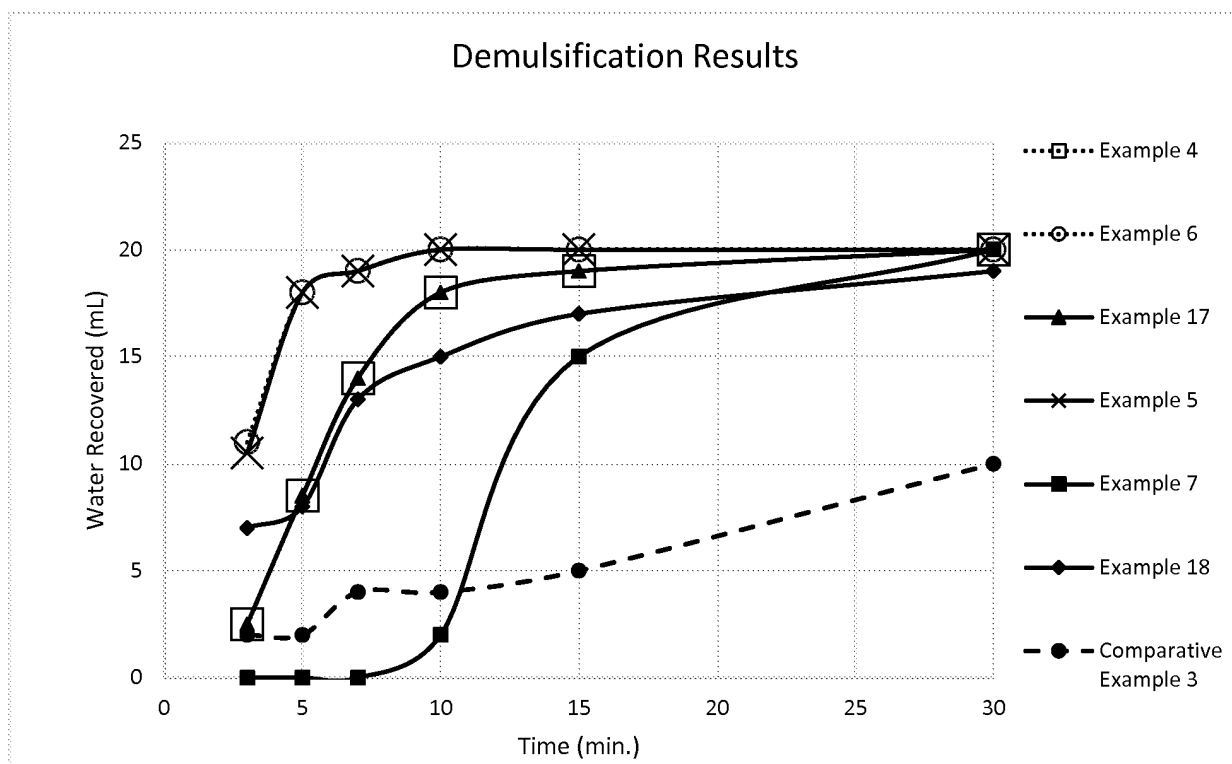


FIG. 1

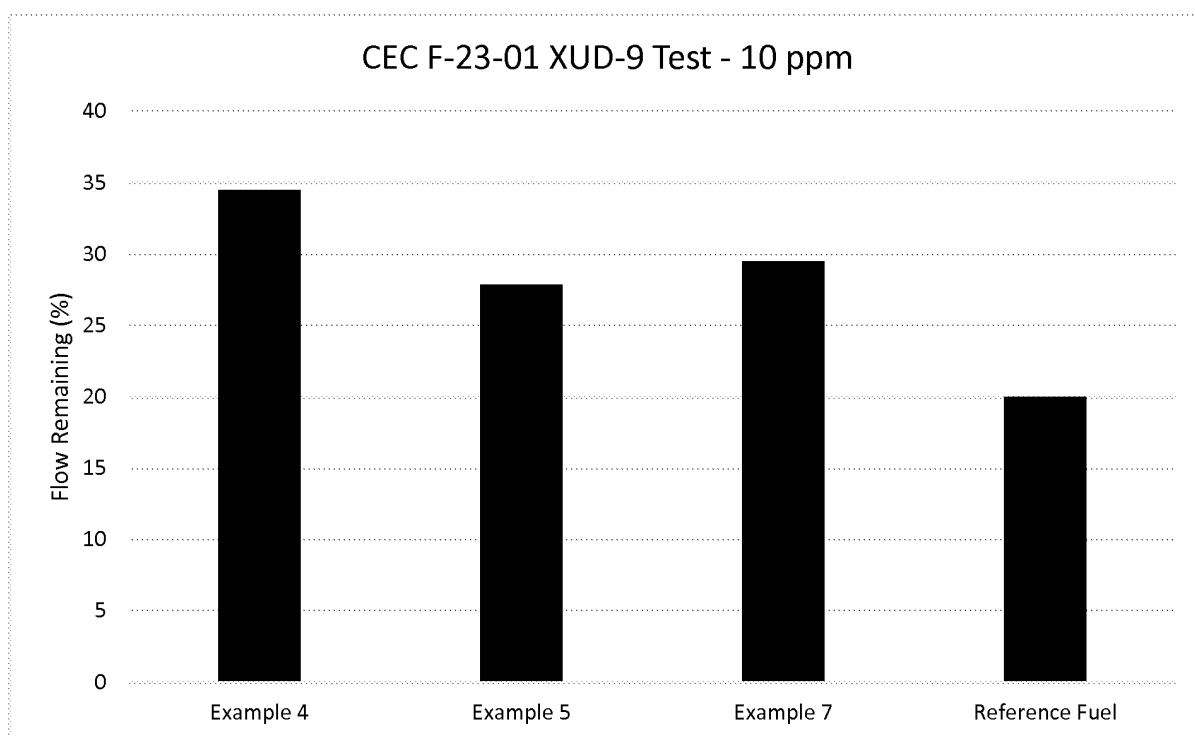


FIG. 2

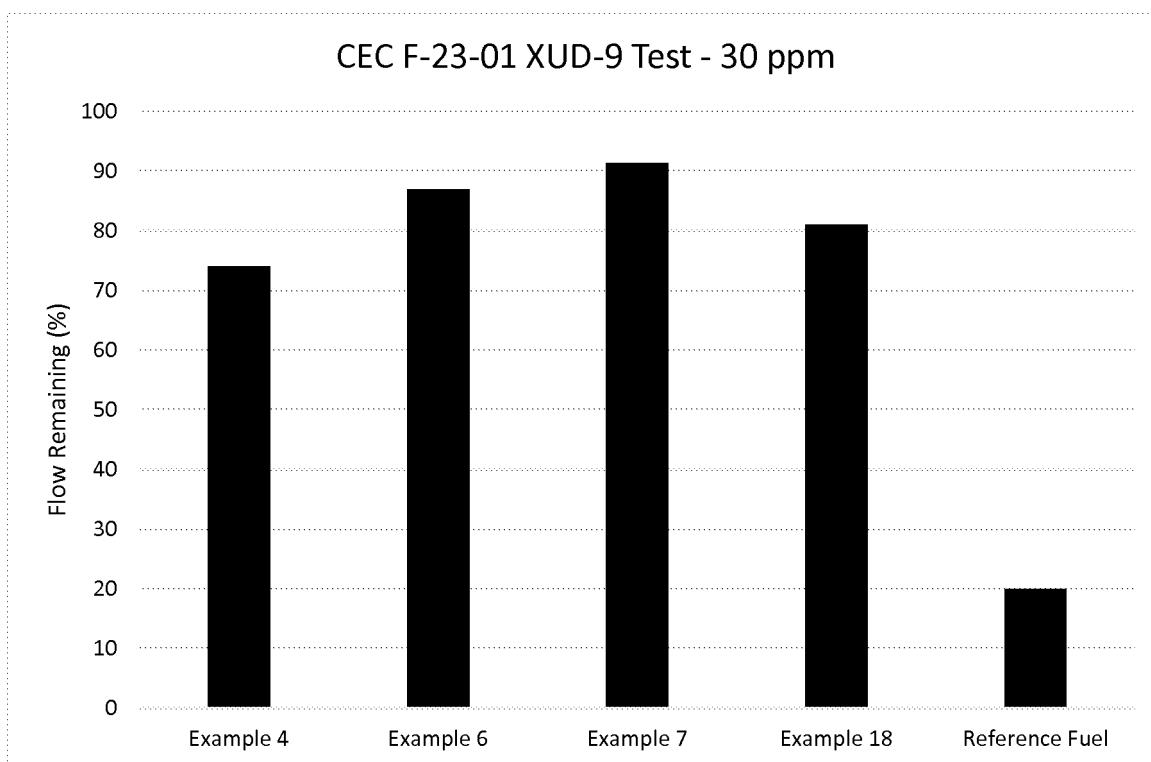


FIG. 3

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20130312318 A1 [0005]
- US 4253980 A [0026]
- US 3778371 A [0026]
- US 4171959 A [0026]
- US 4326973 A [0026]
- US 4338206 A [0026]
- US 5254138 A [0026]
- US 7951211 B [0026] [0088]
- US 3036003 A [0055] [0078]
- US 3236770 A [0055] [0078]
- US 3414347 A [0055] [0078]
- US 3448047 A [0055] [0078]
- US 3461172 A [0055] [0078]
- US 3539633 A [0055] [0078]
- US 3586629 A [0055] [0078]
- US 3591598 A [0055] [0078]
- US 3634515 A [0055] [0078] [0085]
- US 3725480 A [0055] [0078]
- US 3726882 A [0055] [0078]
- US 3980569 A [0055] [0078]
- WO 98004656 A [0056]
- US 6743266 B2 [0056]
- US 20110219674 A [0058] [0088]
- US 4654403 A [0067]
- US 2501731 A [0069]
- US 2616905 A [0069]
- US 2616911 A [0069]
- US 2616925 A [0069]
- US 2777874 A [0069]
- US 3256186 A [0069]
- US 3384585 A [0069]
- US 3365396 A [0069]
- US 3320162 A [0069]
- US 3318809 A [0069]
- US 3488284 A [0069]
- US 3629109 A [0069]
- US 6200936 B [0069]
- US 5688751 A [0069]
- US 4627928 A [0069]
- US 4234435 A [0083]
- US 3172892 A [0083]
- US 3381022 A [0083]
- US 8083814 B [0088]
- US 20130118062 A [0088]
- US 20120010112 A [0088]
- US 20130133243 A [0088]
- US 20080113890 A [0088]
- US 20120149617 A [0088]
- US 20130225463 A [0088]
- US 20110258917 A [0088]
- US 20110315107 A [0088]
- US 20130074794 A [0088]
- US 20120255512 A [0088]
- US 20130333649 A [0088]
- WO 2011141731 A [0088]
- WO 2011095819 A [0088]
- WO 2013017886 A [0088]
- WO 2013070503 A [0088]
- WO 2011110860 A [0088]
- WO 2013017889 A [0088]
- WO 2013017884 A [0088]
- WO 2005054314 A [0100]
- WO 2004035715 A [0102]
- EP 061895 A [0103]
- US 4491455 A [0103]
- EP 261957 A [0105]
- WO 0044857 A [0106]

Non-patent literature cited in the description

- **N. A. PLATÉ ; V. P. SHIBAEV.** Comb-Like Polymers. Structure and Properties. *J. Poly. Sci. Macromolecular Revs.*, 1974, vol. 8, 117-253 [0102]
- Ullmann's Encyclopedia of Industrial Chemistry [0104]