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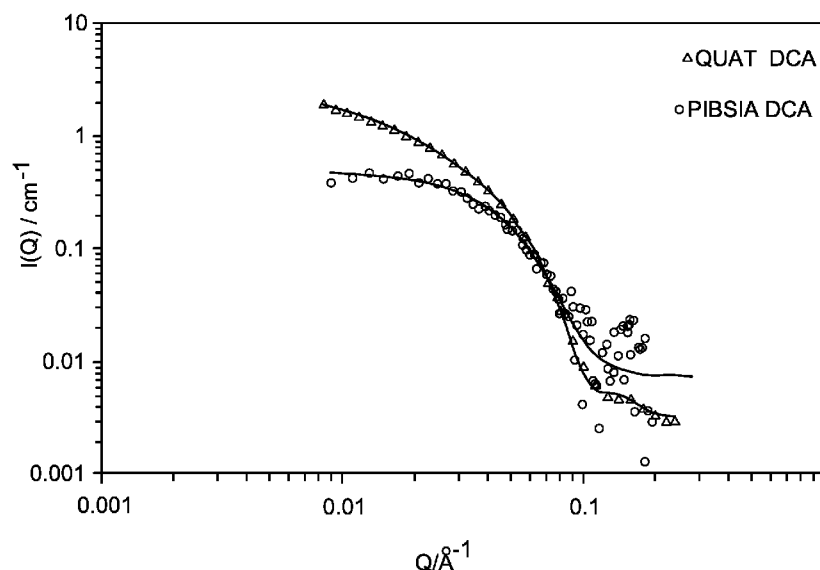


FIG. 2

(57) Abstract: Fuels with a deposit control additive ("DCA") having elliptical micelles to increase the power output of clean engines without deposits, resulting in a "power gain". Diesel fuel compositions with DCA comprising quaternary ammonium salt detergents. Quaternary ammonium salts having non-spherical (ellipsoidal) micelles in a hydrocarbon medium that result in power gain. Elliptical DCAs include DCAs having micelle structures with a minor axis and a major axis wherein the length of the major axis is longer than the length of the minor axis, including micelle shapes that are rod-like, worm-like or thread-like.



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FUEL COMPOSITION WITH REDUCED CAVITATION AND METHODS OF USE

FIELD OF THE INVENTION

[0001] The field of the disclosed technology is generally related to fuel compositions having quaternary ammonium salts.

BACKGROUND OF THE INVENTION

[0002] Hydrocarbon based fuels generally contain numerous deposit-forming substances. When used in internal combustion engines (ICE), deposits from these substances can form on and around constricted areas of the engine which come in contact with the fuel. In diesel engines (and direct injection gasoline engines), the fuel injector tips are particularly prone in deposit formation. The deposits typically form on the fuel injector tips and in the nozzles or spray holes. These injector tip deposits can disrupt the spray pattern of the fuel, potentially causing a reduction in power and fuel economy. Deposit formation in diesel fuel injector nozzles can be highly problematic, resulting in incomplete diesel combustion, and therefore power loss and misfiring.

[0003] 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). IDIDs can cause engines to stall or make them more difficult to start, or even prevent starting entirely

[0004] As deposits form on the injector tips, the flow of fuel through the injectors is reduced and a loss of power can be observed. This observation of "power loss" can be measured by comparing the power output of the engine having the injector deposits with the power output the engine had when it was clean or free of deposits. (Power loss can be measured using the CEC F-98-08 DW10 diesel fuel injector fouling test. The test uses a 2.0 L, 4-cylinder Peugeot DW10 direct injection turbocharged, common rail engine. Other acceptable tests include CEC F-23-01 XUD9 nozzle coking test. The test uses a 1.9 L 4-cylinder Peugeot XUD 9 engine.) While stalling and starting issues are generally more common in engines with IDID, power loss has also been observed in engines with IDID (for example, some John Deere and Cummins engines).

[0005] Modern diesel engines are equipped with high pressure direct injection fuel systems ("HP injector systems") in order to meet the current emissions and fuel economy legislation. These HP injector systems typically operate at greater than >35MPa and have solenoid or piezoelectric valves to control the fuel injection time and quantity, thereby providing better fuel atomization. To lower engine noise, the engine's electronic

control unit can inject a small amount of diesel fuel just before the main injection event ("pilot" injection), thus reducing its explosiveness and vibration, as well as optimizing injection timing and quantity to mitigate variations in fuel quality.

[0006] Detergents, or deposit control additives ("DCA"), may be added to fuels to prevent stalling or starting issues or to recover some of the power lost as a result of the formation of deposits. The detergents typically reduce the amount of power lost (or increase the amount of power recovered) by 1) cleaning-up deposits formed in the injectors and/or 2) keeping deposits from forming in the injectors. The effectiveness of a detergent can be measured by measuring the improvement or reduction in power loss of an engine with deposits. Ideally, effective detergents will result in a complete recovery of power. In other words, the detergent will clean the deposits of a dirty engine such that it has the same power output as a clean engine without deposits.

[0007] Another observed issue HP injector systems is cavitation. Cavitation occurs inside diesel fuel injectors, especially close to the nozzle tip, where the fuel changes direction as it enters the nozzle holes. The change in direction causes low pressure zones close to the injector wall. In these low pressure zones, bubbles or cavities form in the fuel, close to the injector surface. As the cavitation bubbles progress through the injector, they reach higher pressure zones and the bubbles collapse. The imploding or collapsing of these bubbles trigger intense shockwaves and these can damage the injector surface. In severe cases, the shockwaves can cause pitting or spalling that may eventually destroy the injector. Cavitation can also change the effective diameter of the injector holes, thereby effecting the droplet size reducing the efficiency of the injector.

DESCRIPTION OF THE INVENTION

[0008] It was surprisingly found, however, that fuels comprising DCA having elliptical micelles unexpectedly increased the power output of clean engines without deposits, resulting in a "power gain". Studies conducted in an experimental computed tomography ("CT") scanning rig, have shown that diesel fuel with DCA comprising quaternary ammonium salt detergents (hereinafter "quats"), cavitates less than base fuel or base fuel containing other types of detergent, such as a PIBSI type detergent. Analysis of the quats using small-angle neutron scattering ("SANS") showed that these quaternary ammonium salts having non-spherical (ellipsoidal) micelles (hereinafter "ellipsoidal DCA" or "elliptical DCA") in a hydrocarbon medium simulating diesel fuel resulted in power gain. As used herein, "elliptical DCA" or "ellipsoidal DCA" can be any DCA having a non-spherical micelle shape. Elliptical DCAs include DCAs having micelle structures

with a minor axis and a major axis wherein the length of the major axis is longer than the length of the minor axis, including micelle shapes that are rod-like, worm-like or thread-like.

[0009] Without limiting the disclosed technology to one theory of operation, it is believed that the ellipsoidal micelles, under the high shear and high pressure conditions inside diesel injectors, can come together to form rod-like or thread-like structures. These more elongated rod or thread-like structures align themselves in the direction of the flow thus altering the flow characteristics and reducing turbulent flow. This in turn reduces the amount of liquid voids in the fuel and reducing cavitation in the injector. Other DCA, such as traditional PIBSI type deposit control additives and under some conditions, quats form spherical micelles which may explain why they do not result in power gain (hereinafter “spherical DCA”).

[0010] Turning to FIG. 1, it shows an illustration of micelle shapes observed with SANS. The PIBSI type detergent has spherical shaped micelles, whereas the quats have elliptical shaped micelles. Small-angle neutron scattering (SANS) is a technique useful for studying the size and shape of structures in the approximate size range 0.1 to 100 nanometers (nm). SANS experiments are performed using a time-of-flight instrument SANS2D (available at the Science & Technology Facilities Council in Rutherford Appleton, UK). A beam of neutrons is directed at a material (in this case a fuel with a DCA) and the amount of the neutron scattering is measured. The scattering power of different materials (or fuel and DCA) at a specific volume, is determined by the scattering length density (“SLD”) which is isotope dependent. The hydrogen isotopes ^1H and ^2D (deuterium) have very different SLDs, therefore most SANS experiments will use selective deuteration to provide the necessary contrast in the system. In this case n-dodecane- $^2\text{D}_{26}$ (Cambridge Isotope, 98 atom % ^2D) was used as a deuterated surrogate for diesel fuel with dodecane being chemically similar to diesel. In this case the SLD difference arises principally from the contrast step between deuterated solvent and the micelle, so the overall dimensions of the micelle can be elucidated from subsequent data analyses.

[0011] Upon the analyses, SANS profile plots are generated. The SANS profile plots the intensity of scattered neutrons (“ $I(Q)$ ”) against the scattering vector, Q . The observed scattering is dependent on both the wavelength of the incoming neutron radiation (λ) and the scattering angle (θ). Both of these variables can be considered in terms of the scattering vector Q which is plotted on the x-axis. Q is inversely proportional to

the size of the material tested, hence the units of reciprocal length ($\text{\AA}^{-1}$). In other words, the characteristic features of the SANS data for larger materials, or larger micelles, will be shifted to smaller scattering vectors, Q .

[0012] A SANS profile plot for two different fuel detergents, one an elliptical DCA and one a spherical DCA is shown in FIG. 2. To obtain accurate and detailed information this data can be fitted to known mathematical models using a commercially available software package (SasView®) which is a Small Angle Scattering Analysis Software Package. The black lines in FIG. 2 represent the fitted data using this model. The disparity in the data between the elliptical and spherical DCA in FIG. 2 indicates a difference in the micelle shape and size. The PIBSI DCA data fit with the model for spherical micelles with an average minor axis of about 6.9 nm. The quat DCA data, however, fit with the ellipsoid micelle model with an average micelle minor axis of about 6.7 nm and an average micelle length of about 29 nm. The fitted parameters for the lines in FIG. 2 are summarized in Table 1 below.

Table 1

Deposit Control Additive	ppm	Micelle Shape	Length (nm)	Radius (nm)	Axial Ratio
PIBSI	867	Sphere	0.0	3.5	1.0
Quat	885	Cylinder	26.6	4.5	5.0

[0013] Additional SANS profile plots were generated for the quat DCA at different concentrations as shown in FIG. 3. While the ellipsoid micelles are observed at all quat DCA concentrations at 50 ppm actives or above, based on a total weight of the fuel, it appears that concentration can also affect the ellipsoid major axis. The fitted parameters for the concentrations of quat DCA tested are detailed in Table 2.

Table 2

Deposit Control Additive	ppm	Micelle Shape	Length (nm)	Radius (nm)	Axial Ratio
Quat	10	Sphere	6.5	3.6	0.9
Quat	50	Cylinder	9.9	3.7	1.3
Quat	102	Cylinder	12.1	3.7	1.6
Quat	301	Cylinder	16.0	3.8	2.1
Quat	603	Cylinder	34.7	3.5	5.0
Quat	1005	Cylinder	29.2	3.4	4.3

[0014] The results in Table 2 and FIG. 3 show that elliptical micelles are formed at all concentrations between 50 and 1000 ppm with a maximum major axis length at about 600 ppm. It should be noted that these micelle dimensions are determined under static (non-flowing) conditions, but it is possible for elliptical micelles to form at concentrations as low as 10 to 25 ppm under the dynamic flow conditions of an operating injector. In some embodiments, the amount of elliptical DCA present may range from 50 ppm to 5000 ppm, or 50 to 1000 ppm, or 50, to 800, or 80 to 650 ppm actives based on a total weight of the fuel composition.

[0015] Accordingly the major axis may vary. In one embodiment, the major axis may vary from greater than 8 nm to greater than 100, 50, 40, or 30. The minor axis may range from greater than 4 nm to less than or equal to 8 nm, or from about 3 to 4 nm. The ratio of the major axis to the minor axis may be greater than 1 to greater than 100 or greater than 1 to 50. In one embodiment, the ratio of the major axis to the minor axis may range from 1.1 to 8, 7, 6, or 5.

[0016] Under dynamic (flowing conditions), such as those in an injector, these elliptical micelles can come together to form rod-like or thread-like structures as illustrated in FIG. 4. These structures affect the flow of the fuel through the injector, reducing turbulence and increasing laminar flow.

[0017] The quaternary counter ion can have an effect on the on the micelle shape and size. Table 3 shows that when the counter ion is small, as in the case of the acetate ion or dimethyl sulfate, cylinder micelles are formed, but with a TOFA counter ion vesicles and spheres are formed.

Table 3

Deposit Control Additive Counter ion	ppm	Micelle Shape	Length (nm)	Radius (nm)	Axial Ratio
Acetate	301	Cylinder	16.0	3.8	2.1
Acetate	603	Cylinder	34.7	3.5	5.0
Acetate	885	Cylinder	26.6	4.5	5.0
DMS	424	Cylinder	13.1	3.7	1.8
DMS	844	Cylinder	13.6	3.8	1.8
DMS	1410	Cylinder	14.0	3.9	1.8
Deposit Control Additive Counter ion	ppm	Micelle Shape	Vesicle Core Radius (nm)	Vesicle Thickness (nm)	Sphere Radius (nm)
TOFA	304	Vesicle + sphere	5.0	7.2	3.0
TOFA	604	Vesicle + sphere	4.5	7.6	3.0
TOFA	1011	Vesicle + sphere	5.2	6.7	3.0

[0018] It is believed that these rod-like or thread-like structures reduce the amount of liquid voids in the fuel thereby reducing cavitation in the injector and increasing the liquid fraction, i.e. the amount of liquid fuel, passing through the injector outlet holes.

Tests simulating injector conditions using a CT device show that the liquid fraction of a fuel comprising elliptical DCA passing through the injector outlets can increase as compared to fuels having spherical DCA. Turning to FIG.5, it shows the liquid fraction observed passing through an injector using CT scanning. FIG 5a shows the liquid fraction of a fuel having a spherical DCA (PIBSI detergent). FIG. 5b shows the liquid fraction of a fuel having an elliptical DCA ("DCA quat"). The liquid fraction of the fuel having the DCA quat is greatly increased around the surface of the inside walls of injector and surface of the injector holes, resulting in power gain.

[0019] The DCA quats having elliptical micelles, or elliptical DCA may be any quaternary ammonium salt. Exemplary DCA quats include, but are not limited to, imide, amide, or ester quats.

[0020] The imide quats may comprises the reaction product of (a) the reaction of a hydrocarbyl substituted acylating agent and a compound having an oxygen or nitrogen

atom capable of condensing with the acylating agent and further having a tertiary amino group; and (b) a quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen.

[0021] 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:

[0022] 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);

[0023] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this technology, 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);

[0024] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this technology, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; alternatively, there may be no non-hydrocarbon substituents in the hydrocarbyl group.

[0025] The amide or ester quats may comprise the reaction product of (a) a non-quaternized amide or ester detergent having a tertiary amine functionality; and (b) a quaternizing agent. The amide or ester detergents may be derived from non-quaternized polyisobutylsuccinamides or esters having a tertiary amine functionality and an amide or ester group.

[0026] The quaternizing agents may be a dialkyl sulfates, alkyl halides, hydrocarbyl substituted carbonates, hydrocarbyl epoxide, hydrocarbyl epoxides in combination with an acid, carboxylates, alkyl esters, or mixtures thereof.

[0027] The hydrocarbyl substituted acylating agents may be, for example, polyisobutyl succinic acids or anhydrides. These acids or anhydrides may have a number av-

erage (M_n) molecular weight of any value as measured using gel permeation chromatography (GPC) based on polystyrene standards. In one embodiment, the M_n may range from 180 to 3000, or 250 to 1000, or 300 to 750. In one embodiment, the quat may have an M_n ranging from 300 to 750. The number average molecular weight of the materials described herein is measured using gas permeation chromatography (GPC) using a Waters GPC 2000 equipped with a refractive index detector and Waters EmpowerTM data acquisition and analysis software. The columns are polystyrene (PLgel, 5 micron, available from Agilent/Polymer Laboratories, Inc.). For the mobile phase, individual samples are dissolved in tetrahydrofuran and filtered with PTFE filters before they are injected into the GPC port.

Waters GPC 2000 Operating Conditions:

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

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

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

[0028] In one embodiment, the DCA quat is an amide/ester quat comprising the reaction product of (a) a quaternizable compound that is the reaction product of a hydrocarbyl-substituted acylating agent, wherein the hydrocarbyl-substituent has a number average molecular weight ranging from 300 to 750, and a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with the hydrocarbyl-substituted acylating agent to form an ester or amide, and further having at least one quaternizable amino group; and (b) a quaternizing agent suitable for converting the quaternizable amino group of the nitrogen containing compound to a quaternary nitrogen.

The Hydrocarbyl Substituted Acylating Agent

[0029] The hydrocarbyl substituted acylating agent employed to prepare the quaternizable compound can be the reaction product of the precursor to the hydrocarbyl-substituent, which is a long chain hydrocarbon, generally a polyolefin, with a monounsaturated carboxylic acid reactant such as (i) α,β -monounsaturated C₄ to C₁₀ dicarboxylic acid such as fumaric acid, itaconic acid, maleic acid.; (ii) derivatives of (i) such as

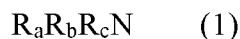
anhydrides or C₁ to C₅ alcohol derived mono- or di-esters of (i); (iii) α,β -monounsaturated C₃ to C₁₀ monocarboxylic acid such as acrylic acid and methacrylic acid.; or (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived esters of (iii).

[0030] The hydrocarbyl-substituent can be derived from polybutene, that is, polymers of C₄ olefins, including 1-butene, 2-butene and isobutylene. C₄ polymers can include polyisobutylene.

Nitrogen Containing Compound

[0031] The composition of the present technology contains a nitrogen containing compound having a 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.

[0032] In some embodiments, the quaternizable nitrogen containing compound may be tertiary amines of formula (1).



[0033] The tertiary amine (1) preferably bears a segment of the formula $NR_a R_b$ where one of the radicals has an alkyl group having 8 to 40 carbon atoms and the other an alkyl group having up to 40 and more preferably 8 to 40 carbon atoms. The R_c radical is especially a short-chain C₁-C₆-alkyl radical, such as a methyl, ethyl or propyl group. R_a and R_b may be straight-chain or branched, and/or may be the same or different. For example, R_a and R_b may be a straight-chain C₁₂-C₂₄-alkyl group. Alternatively, only one of the two radicals may be long-chain (for example having 8 to 40 carbon atoms), and the other may be a methyl, ethyl or propyl group.

[0034] Appropriately, the $NR_a R_b$ segment is derived from a secondary amine, such as dioctadecylamine, dicocoamine, hydrogenated ditallowamine and methylbehenylamine. Amine mixtures as obtainable from natural materials are likewise suitable. One example is a secondary hydrogenated tallowamine where the alkyl groups are derived from hydrogenated tallow fat, and contain about 4% by weight of C₁₄, 31% by weight of C₁₆ and 59% by weight of C₁₈-alkyl groups. Corresponding tertiary amines of the formula (3) are sold, for example, by Akzo Nobel under the Armeen® M2HT or Armeen® M2C name.

[0035] The tertiary amine (3) may also take such a form that the R_a , R_b and R_c radicals have identical or different long-chain alkyl radicals, especially straight-chain or branched alkyl groups having 8 to 40 carbon atoms.

[0036] Examples of the nitrogen containing compound capable of reacting with the acylating agent can include, but are not limited to, dimethylaminopropylamine, N,N-dimethyl-aminopropylamine, N,N-diethyl-aminopropylamine, N,N-dimethyl-aminoethylamine ethylenediamine, 1,2-propylenediamine, 1,3-propylene diamine, isomeric amines, including butylenediamines, pentanediamines, hexanediamines, and heptanediamines, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexamethylenetetramine, and bis(hexamethylene) triamine, the diaminobenzenes, the diaminopyridines, N-methyl-3-amino-1-propylamine, or mixtures thereof. The nitrogen containing compounds capable of reacting with the acylating agent and further having a quaternizable amino group can further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, 3'3'-iminobis(N,N-dimethylpropylamine). Additional nitrogen containing compounds capable of reacting with the acylating agent and having a quaternizable amino group include alkanolamines including but not limited to triethanolamine, trimethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, N,N,N-tris(hydroxyethyl)amine, N,N,N-tris(hydroxymethyl)amine, N,N-dimethylethanolamine, N,N-diethylethanolamine, 2-(diisopropylamino)ethanol, 2-(dibutylamino)ethanol, 3-dimethylamino-1-propanol, 3-diethylamino-1-propanol, 1-dimethylamino-2-propanol, 1-diethylamino-2-propanol, 2-dimethylamino-2-methyl-1-propanol, 5-dimethylamino-2-propanol, 2-[2-(dimethylamino)ethoxy]-ethanol, 4-methyl-2-{piperidino methyl}phenol, 1-benzyl-3-pyrrolidinol, 1-benzylpyrrolidine-2-methanol, 2,4,6-tri(dimethylaminomethyl)phenol, dialkoxylated amines such as Ethermeen T12. In some embodiments, the nitrogen containing compound excludes dimethylaminopropylamine.

[0037] Further non-limiting examples of suitable amines are N,N-dimethyl-N-(2-ethylhexyl)amine, N,N-dimethyl-N-(2-propylheptyl)amine, dodecyl-dimethylamine, hexadecyldimethylamine, oleyldimethylamine, cocoyldimethylamine, dicocoylmethylamine, tallowdimethylamine, ditallowmethylamine, tridodecylamine, trihexadecylamine, trioctadecylamine, soyadimethylamine, tris(2-ethylhexyl)amine, and Alamine 336 (tri-n-octylamine), or combinations thereof.

Quaternizable Compound

[0038] The hydrocarbyl substituted acylating agents and nitrogen containing compounds described above are reacted together to form a quaternizable compound. Methods and

processes for reacting the hydrocarbyl substituted acylating agents and nitrogen containing compounds are well known in the art.

[0039] In some embodiments, the reaction between the hydrocarbyl substituted acylating agents and nitrogen containing compounds can be carried out at temperatures of less than about 80°C, such as between about 30 and about 70 or 75°C, or about 40 and about 60°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.

[0040] 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) 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

[0041] The quaternary ammonium salt can be formed when the quaternizable compound, that is, the reaction products of the hydrocarbyl substituted acylating agent and nitrogen containing compounds described above, are reacted with a quaternizing agent. Suitable quaternizing agents can include, for example, dialkyl sulfates, alkyl halides, hydrocarbyl substituted carbonates, hydrocarbyl epoxides, carboxylates, alkyl esters, and mixtures thereof.

[0042] In one embodiment, the quaternizing agent can include alkyl halides, such as chlorides, iodides or bromides, alkyl sulfonates, dialkyl sulfates, such as, dimethyl sulfate and diethyl sulfate, sultones, alkyl phosphates, such as, C₁₋₁₂ trialkylphosphates, di C₁₋₁₂ alkylphosphates, borates, C₁₋₁₂ alkyl borates, alkyl nitrites, alkyl nitrates, dialkyl carbonates, such as dimethyl oxalate, alkyl alkanoates, such as methylsalicylate, O,O-di-C₁₋₁₂ alkyldithiophosphates, or mixtures thereof.

[0043] In one embodiment, the quaternizing agent may be derived from dialkyl sulfates such as dimethyl sulfate or diethyl sulfate, N-oxides, sultones such as propane and butane sultone, alkyl, acyl or aryl halides such as methyl and ethyl chloride, bromide or iodide or benzyl chloride, and a hydrocarbyl (or alkyl) substituted carbonates. If the alkyl halide is benzyl chloride, the aromatic ring is optionally further substituted with alkyl or alkenyl groups.

[0044] The hydrocarbyl (or alkyl) groups of the hydrocarbyl substituted carbonates may contain 1 to 50, 1 to 20, 1 to 10 or 1 to 5 carbon atoms per group. In one embodiment, the hydrocarbyl substituted carbonates contain two hydrocarbyl groups that may be the same or different. Examples of suitable hydrocarbyl substituted carbonates include dimethyl or diethyl carbonate.

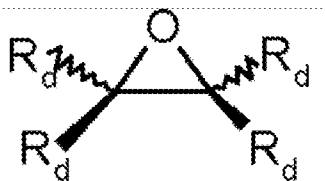
[0045] In another embodiment, the quaternizing agent can be a hydrocarbyl epoxide. Examples of hydrocarbyl epoxides include ethylene oxide, propylene oxide, butylene oxide, styrene oxide and combinations thereof.

[0046] In yet other embodiments, the quaternizing agent is selected from alkylene oxides, optionally in combination with acid; aliphatic or aromatic carboxylic esters such as, more particularly, dialkyl carboxylates; alkanoates; cyclic nonaromatic or aromatic carboxylic esters; alkyl sulfates; alkyl halides; alkylaryl halides; dialkyl carbonates; and mixtures thereof.

[0047] Suitable examples are alkyl esters, derived from carboxylic acids, whose pK_a is less than 3.5. Examples are especially alkyl esters derived from oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic acid and citric acid. In yet other embodiments, the quaternizing agents are the lower alkyl esters of salicylic acid, such as methyl salicylate, ethyl salicylate, n- and i-propyl salicylate, and n-, i- or tert-butyl salicylate.

[0048] The above-mentioned esters are typically used in the presence of acids, especially in the presence of free protic acids such as, in particular, with C_{1-12} -monocarboxylic acids such as formic acid, acetic acid or propionic acid, or C_{2-12} -dicarboxylic acids such as oxalic acid or adipic acid; or else in the presence of sulfonic acids such as benzenesulfonic acid or toluenesulfonic acid, or aqueous mineral acids such as sulfuric acid or hydrochloric acid.

[0049] In a further particular embodiment, the at least one quaternizable tertiary nitrogen atom is quaternized with at least one quaternizing agent selected from epoxides, especially hydrocarbyl epoxides.



where the R_d radicals present therein are the same or different and are each H or a hydrocarbyl radical, where the hydrocarbyl radical has at least 1 to 10 carbon atoms. These are especially aliphatic or aromatic radicals, for example linear or branched C_{1-10} -alkyl radicals, or aromatic radicals such as phenyl or C_{1-4} -alkylphenyl.

[0050] Examples of suitable hydrocarbyl epoxides include aliphatic and aromatic alkylene oxides such as, more particularly, C₂₋₁₂-alkylene oxides such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, 2-methyl-1,2-propene oxide (isobutene oxide), 1,2-pentene oxide, 2,3-pentene oxide, 2-methyl-1,2-butene oxide, 3-methyl-1,2-butene oxide, 1,2-hexene oxide, 2,3-hexene oxide, 3,4-hexene oxide, 2-methyl-1,2-pentene oxide, 2-ethyl-1,2-butene oxide, 3-methyl-1,2-pentene oxide, 1,2-decene oxide, 1,2-dodecene oxide or 4-methyl-1,2-pentene oxide; and aromatic-substituted ethylene oxides such as optionally substituted styrene oxide, especially styrene oxide or 4-methylstyrene oxide.

[0051] In the case of use of epoxides as quaternizing agents, these are used in the presence or in the absence of free acids, especially in the presence or absence of free protic acids, such as, in particular, with C₁₋₁₂-monocarboxylic acids such as formic acid, acetic acid or propionic acid, or C₂₋₁₂-dicarboxylic acids such as oxalic acid or adipic acid; or else in the presence or absence of sulfonic acids such as benzenesulfonic acid or toluenesulfonic acid, or aqueous mineral acids such as sulfuric acid or hydrochloric acid. The quaternization product thus prepared is thus either "acid-containing" or "acid-free" in the context of the present invention.

[0052] The free protic acid may be selected from a wide variety of cyclic and non-cyclic anhydrides and their acid analogues, including, but not limited to, acetic anhydride, oxalic anhydride, propionic anhydride, butyric anhydride, isobutyric anhydride, 4-pentanoic anhydride, valeric anhydride, isovaleric anhydride, trimethylacetic anhydride, hexanoic anhydride, maleic anhydride, malonic anhydride, 2-methylacrylic anhydride, succinic anhydride, dodecyl succinic anhydride, polyisobutenyl succinic anhydride, glutaric anhydride, cyclohexanecarboxylic anhydride, 1-cyclopentene-1,2-dicarboxylic anhydride, cyclobutane-1,2,3,4-tetracarboxylic dianhydride, benzoic anhydride, phthalic anhydride, naphthalenetetracarboxylic dianhydride, methyltetrahydrophthalic anhydride, pyromellitic dianhydride, trimellitic anhydride, and the like.

[0053] The free protic acid may also include carboxylic acids such as C₁₋₁₂-monocarboxylic acids such as formic acid, acetic acid or propionic acid, or C₂₋₁₂-dicarboxylic acids such as oxalic acid or adipic acid; or else in the presence of sulfonic acids such as benzenesulfonic acid or toluenesulfonic acid, or aqueous mineral acids such as sulfuric acid or hydrochloric acid.

[0054] In yet other embodiments, the DCA quat may 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 .

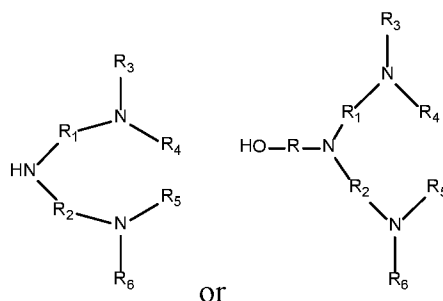
5 **[0055]** In an embodiment, the salts are prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of 1300 to 3000 is an imide. In an embodiment, the quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number
10 average molecular weight of greater than 1200 M_n or having a hydrocarbyl substituent with a number average molecular weight of 300 to 750 is an amide or ester.

[0056] 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,
15 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.

[0057] The hydrocarbyl substituted acylating agent may also be a copolymer formed by
20 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
25 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.

[0058] 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
30 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.

[0059] In an embodiment the nitrogen containing compound of the salt is an imidazole or nitrogen containing compound of either of formulas.

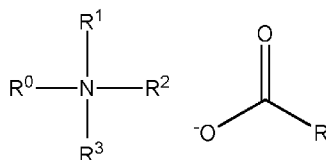


wherein R may be a C₁ to C₆ alkylene group; each of R₁ and R₂, individually, may be a C₁ to C₆ hydrocarbylene group; and each of R₃, R₄, R₅, and R₆, individually, may be a hydrogen or a C₁ to C₆ hydrocarbyl group. In one embodiment R₁ or R₂ can be, for example, a C₁, C₂ or C₃ alkylene group. In the same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

[0060] 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 may be an alcohol functionalized epoxide or C₄ to C₁₄ epoxide. In yet another embodiment, the hydrocarbyl epoxide may be an alcohol functionalized epoxide or C₄ to C₂₀ epoxide.

[0061] In some embodiments, the quaternizing agent is multi-functional resulting in the additional quaternary ammonium salts being a coupled quaternary ammoniums salts.

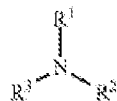
[0062] Additional quaternary ammonium salts include, but are not limited to quaternary ammonium salts having a hydrophobic moiety in the anion. Exemplary compounds include quaternary ammonium compounds having the formula below:



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.

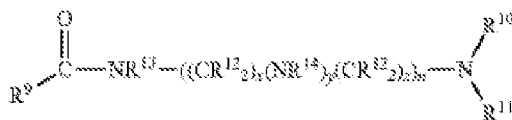
[0063] Additional quaternary ammonium salts may also include polyetheramines that are the reaction products of a polyether-substituted amine comprising at least one tertiary quaternizable amino group and a quaternizing agent that converts the tertiary amino group to a quaternary ammonium group.

- 5 [0064] In yet other embodiments, the quaternary ammonium salt may be made by reacting a tertiary amine of the formula



wherein each of R^1 , R^2 , and R^3 is selected from hydrocarbyl groups containing from 1 to 200 carbon atoms, such as from 1 to 50 carbon atoms, or from 1 to 24 carbon atoms, with a carboxylic acid containing from 1 to 200 carbon atoms and a quaternizing agent and an anhydride to provide an esterified alkoxylated quaternary ammonium salt. In another embodiment the reaction to make the quaternary ammonium salt may be conducted in the presence of a protonating agent having an acid dissociation constant (pK_a) of less than about 13, such as a carboxylic acid or an alkyl phenol. The esterified quaternary ammonium salt may be made from the quaternary ammonium salt and an anhydride. The anhydride may be selected from cyclic and non-cyclic anhydrides including, but not limited to, acetic anhydride, polyisobutenyl succinic anhydride and hydrocarbyl alkylene anhydride. The alkoxylated quaternary ammonium salt may also be derived from an amido amine and a quaternizing agent in the presence of a protonating agent and anhydride. The protonating agent may be obtained from a carboxylic acid, alkyl phenol or from the amido amine derived from a fatty acid wherein the reaction product containing the amido amine has an acid number ranging from about 1 to about 200 mg KOH/g. Regardless of how the esterified alkoxylated quaternary ammonium salt is made, a key feature of the disclosure is that the amine contains at least one tertiary amino group.

[0065] In one embodiment, a tertiary amine including diamines and polyamines may be reacted with a C_1 to C_{54} carboxylic acid to form an amido amine and the amido amine may be subsequently reacted with a quaternizing agent. Suitable tertiary amido amine compounds of the formula



may be used, wherein each of R^{10} , and R^{11} is selected from hydrocarbyl groups containing from 1 to 50 carbon atoms, each R^9 , R^{12} , R^{13} and R^{14} may be independently selected from hydrogen or a hydrocarbyl group, x may range from 1 to 6, y may be 0 or 1, z may be 1 to 6, and n may range from 1 to 6. Each hydrocarbyl group R^9 to R^{14} may independently be linear, branched, substituted, cyclic, saturated, unsaturated, or contain one or more hetero atoms. Suitable hydrocarbyl groups may include, but are not limited to alkyl groups, aryl groups, alkylaryl groups, arylalkyl groups, alkoxy groups, aryloxy groups, amino groups, and the like. Particularly suitable hydrocarbyl groups may be linear or branched alkyl groups. A representative example of an amine reactant which may be amidized and quaternized to yield compounds disclosed herein include for example, but are not limited to, dimethyl amino propyl amine.

[0066] If the amine contains any primary or secondary amino groups, it may be desirable to alkylate the primary or secondary amino groups to a tertiary amino group prior to quaternizing the amido amine. In one embodiment, alkylation of primary amines and secondary amines or mixtures with tertiary amines may be exhaustively or partially alkylated to a tertiary amine and further alkoxylated to a quaternary salt.

[0067] When the amine has a primary or secondary amine group, the amine may be converted to an amido amine by reacting the amine with a C_1 to C_{54} carboxylic acid.

The acid may be a monoacid, a dimer acid, or a trimer acid. The acid may be selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, 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, docosahexaenoic acid, and the dimer and trimer acids thereof. When reacted with the amine, the reaction product may be a C_1 - C_{54} -alkyl or alkenyl-substituted amido amine such as a C_1 - C_{54} -alkyl or alkenyl-substituted amido propyldimethylamine.

[0068] The anhydride used to make the esterified quaternary ammonium salt may be selected from a wide variety of cyclic and non-cyclic anhydrides, including, but not limited to, acetic anhydride, oxalic anhydride, propionic anhydride, butyric anhydride,

isobutyric anhydride, 4-pentanoic anhydride, valeric anhydride, isovaleric anhydride, trimethylacetic anhydride, hexanoic anhydride, maleic anhydride, malonic anhydride, 2-methylacrylic anhydride, succinic anhydride, dodecyl succinic anhydride, polyisobutenyl succinic anhydride, glutaric anhydride, cyclohexanecarboxylic anhydride, 1-cyclopentene-1,2-dicarboxylic anhydride, cyclobutane-1,2,3,4-tetracarboxylic dianhydride, benzoic anhydride, phthalic anhydride, naphthalenetetracarboxylic dianhydride, methyltetrahydrophthalic anhydride, pyromellitic dianhydride, trimellitic anhydride, and the like. The mole ratio of anhydride to tertiary amine may range from about 5:1 to about 1:5, such as 2:1 to 1:2 or from 0.8:1 to 1.2:1.

[0069] The esterified quaternary ammonium salts from tertiary amines may be made in one stage or two stages. The reaction may be carried out by contacting and mixing the tertiary amine with the olefin oxide in the reaction vessel wherein a carboxylic acid and an anhydride are added to the reaction mixture. In an alternative embodiment, the anhydride may be reacted with the quaternary ammonium salt in a separate reaction step to provide the esterified quaternary ammonium salt. In the two step reaction sequence, the protonating agent may be selected from either a carboxylic acid or phenol. In the one step reaction process, the protonating agent is selected from a carboxylic acid.

[0070] The carboxylic acid may be same acid used to make the amido amine or may be selected from any of the above listed carboxylic acids, fatty acids, formic acid, acetic acid, propionic acid, butyric acid, C₁-C₂₀₀ polymeric acid and mixtures thereof, such a polyolefinic mono- or di-carboxylic acid, polymeric polyacids and mixtures thereof, and the like. When used, the mole ratio of protonating agent per mole of epoxy equivalents added to the reaction mixture may range from about 1:5 to 5:1, for example from about 1:2 to about 2:1 moles of acid per mole of epoxy equivalents. In one embodiment, the anion of the quaternary ammonium salt is a carboxylate anion.

[0071] The reaction may be carried out at temperature ranging from about 30° to about 90° C., for example from about 45° to about 70° C. The reaction may be conducted by reacting any amount of tertiary amino groups to epoxy groups sufficient to provide a quaternary ammonium compound. In one embodiment a mole ratio of tertiary amino groups to epoxy groups may range from about 2:1 to about 1:2. When the reaction is completed volatiles and unreacted reagents may be removed from the reac-

tion product by heating the reaction product under vacuum. The product may be diluted with mineral oil, diesel fuel, kerosene, or an inert hydrocarbon solvent to prevent the product from being too viscous, if necessary.

Additive Packages

5 **[0072]** The DCA quats described herein may be used with other additives performance additives in an additive package for use with a fuel, such as diesel fuel. Such additional performance additives can be added to any fuel depending on the results desired and the application in which the composition will be used.

10 **[0073]** Although any type of additional performance additive may be used, with the DCA quats described herein, the following additional additives are particularly useful for fuel: 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-
15 hydrate inhibitors, or any combination thereof.

20 **[0074]** Demulsifiers suitable for use with the DCA 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
25 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;
30 and 3,980,569 herein incorporated by reference. Other suitable demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene oxide (EO) and propylene oxide (PO), for example including in the form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. In an embodiment there is

no demulsifier present in the fuel. The demulsifiers may be used alone or in combination. Some demulsifiers are commercially available, for example from Nalco or Baker Hughes.

[0075] 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.

[0076] 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.

[0077] The additional performance additives, which may be present in the fuel, also include di-ester, di-amide, ester-amide, and ester-imide friction modifiers prepared by reacting an α -hydroxy acid with an amine and/or alcohol optionally in the presence of a known esterification catalyst. Examples of α -hydroxy acids include glycolic acid, lactic acid, α -hydroxy dicarboxylic acid (such as tartaric acid) and/or an α -hydroxy tricarboxylic acid (such as citric acid), with an amine and/or alcohol, optionally in the presence of a known esterification catalyst. These friction modifiers, often derived from tartaric acid, citric acid, or derivatives thereof, may be derived from amines and/or alcohols that are branched,

resulting in friction modifiers that themselves have significant amounts of branched hydrocarbyl groups present within its structure. Examples of suitable branched alcohols used to prepare such friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, and mixtures thereof. Friction modifiers may be present at 0 to 6 wt % or 0.001 to 4 wt %, or 5 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 %.

[0078] 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 10 detergent/dispersant may be a polyisobutenyl substituted succinic acid, amide or ester, wherein the polyisobutenyl substituent has a number average molecular weight of 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. In one embodiment, the additional detergent/dispersant may be quaternary ammonium salts other than that of the present technology.

[0079] In yet other embodiments, the compositions may further comprise a hydrolyzed succinic acid or anhydride. The hydrolyzed succinic acid or anhydride may have a M_n ranging 20 from 225 to 1000. In another embodiment, the hydrolyzed succinic acid or anhydride may have a M_n of 1000 and more than 70 mole% vinylidene groups ("high-vinylidene"). In another embodiment, the hydrolyzed succinic acid or anhydride may have a M_n of 550 and between 20 mole% and 70 mole% vinylidene groups ("mid-vinylidene"). In yet other embodiments the hydrolyzed succinic acid or anhydride may have a M_n of less than 550 and less than 25 mole% vinylidene groups ("conventional vinylidene").

[0080] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the fuel and/or lubricant compositions of this invention. Viscosity improvers are usually polymers, including polyisobutenes, polymethacrylates (PMA) and polymethacrylic acid esters, hydrogenated diene polymers, 30 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.

[0081] Multifunctional viscosity improvers, which also have dispersant and/or antioxidant properties are known and may optionally be used in the fuel and/or lubricant compositions. Dispersant viscosity modifiers (DVM) are one example of such multifunctional additives. DVM are typically prepared by copolymerizing a small amount of a nitrogen-containing monomer with alkyl methacrylates, resulting in an additive with some combination of dispersancy, viscosity modification, pour point depressancy and dispersancy. Vinyl pyridine, N-vinyl pyrrolidone and N,N'-dimethylaminoethyl methacrylate are examples of nitrogen-containing monomers. Polyacrylates obtained from the polymerization or copolymerization of one or more alkyl acrylates also are useful as viscosity modifiers.

[0082] Foam inhibitors that may be useful in fuel and/or lubricant compositions of the invention include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. The disclosed technology may also be used with a silicone-containing antifoam agent in combination with a C₅ – C₁₇ alcohol.

[0083] Pour point depressants that may be useful in fuel and/or lubricant compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0084] Exemplary additive package compositions are included in Table 4. The amounts shown are in weight percents, based on a total weight of the additive package.

Table 4

	Additive Package A	Additive Package B	Additive Package C	Additive Package D	Additive Package E
DCA Quat	5 to 20	10 to 30	10 to 30	10 to 30	30 to 45
Hydrolyzed PIBSA	10 to 20	5 to 15	5 to 15	5 to 15	10 to 20
Commercial de-mulsifier	1 to 2	2 to 6	2 to 6	2 to 4	1 to 2
Polydimethyl siloxane foam inhibitor	0.5 to 1.5	1 to 3	2 to 3	0.5 to 1	0
Aromatic 150 solvent	50 to 70	60 to 80	60 to 80	55 to 70	30 to 40
Ethyl hexyl alcohol	5 to 20	0	0	5 to 10	10 to 20

Fuel

- 5 **[0085]** The compositions of the present technology 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, the fuel is a gasoline, and in other embodiments the fuel is a leaded gasoline, or a nonleaded gasoline. In another embodiment, 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.
- 10 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 other embodiments, 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
- 25

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.

[0086] Except in the examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." 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 disclosed element can be used together with ranges or amounts for any of the other elements.

[0087] 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 basic and novel characteristics of the composition or method under consideration.

What is claimed is:

1. A fuel composition comprising a deposit control additive having elliptical micelles (“elliptical DCA”).

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2. The composition of claim 1, wherein said elliptical micelles have a major axis and a minor axis and wherein a ratio of the major axis to minor axis ranges from greater than 1 to greater than 20 or greater than 1 to 10 or greater than 1 to greater than 5.

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3. The composition of claim 1 or 2, wherein said fuel is diesel or gasoline.

4. The composition of any of claims 1 to 3, wherein said elliptical DCA comprises a quaternary ammonium salt (“quat”).

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5. The composition of claim 4, wherein said quat comprises an amide, ester, or imide containing quat is the reaction product of:

a) a quaternizable compound that is the reaction product of:

(i) a hydrocarbyl-substituted acylating agent, and

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(ii) a nitrogen containing compound having an oxygen or nitrogen atom capable of reacting with said hydrocarbyl-substituted acylating agent to form an amide, ester or imide, and further having at least one quaternizable amino group; and

b) a quaternizing agent suitable for converting the quaternizable amino

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group of the nitrogen containing compound to a quaternary nitrogen.

6. The composition of claim 5, wherein said hydrocarbyl-substituent has a number average molecular weight ranging from 180 to 3000, or 250 to 1000, or 300 to 750.

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7. The composition of any of claims 1 to 6, wherein said elliptical DCA is present at an amount ranging from at least 50 ppm to 5000 ppm, or 50 to 1000 ppm, or 50, to 800, or 80 to 650 ppm actives based on a total weight of said fuel composition.

8. A method of reducing cavitation in the injector of an engine, said method comprising fueling said engine using the composition as in any of claims 1 to 7.

9. The method of claim 8, wherein said cavitation is reduced by at least 1 % to 20 % as compared to fueling said engine using a deposit control additive having spherical micelles (“spherical DCA”).

10. The method of claim 9, wherein said cavitation is reduced by at least 5 % to at least 10 %.

11. A method of increasing the liquid fraction of fuel passing through the direct injector of an engine, said method comprising fueling said engine using the composition as in any of claims 1 to 7.

12. The method of claim 11, wherein said liquid fraction is increased by at least 1 % to 20 % as compared to fueling said engine using a deposit control additive having spherical micelles (“spherical DCA”).

13. The method of claim 12, wherein said liquid fraction is increased by at least 1 % to at least 10 % or 5 %.

14. The method of any of claims 8 to 13, wherein said engine is a diesel or gasoline direct injection engine.

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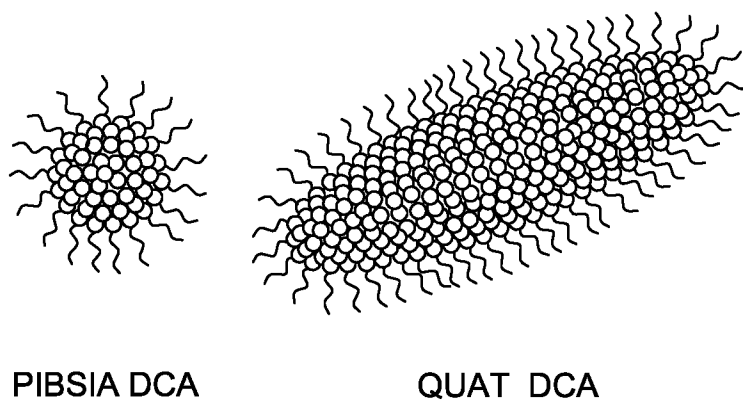


FIG. 1

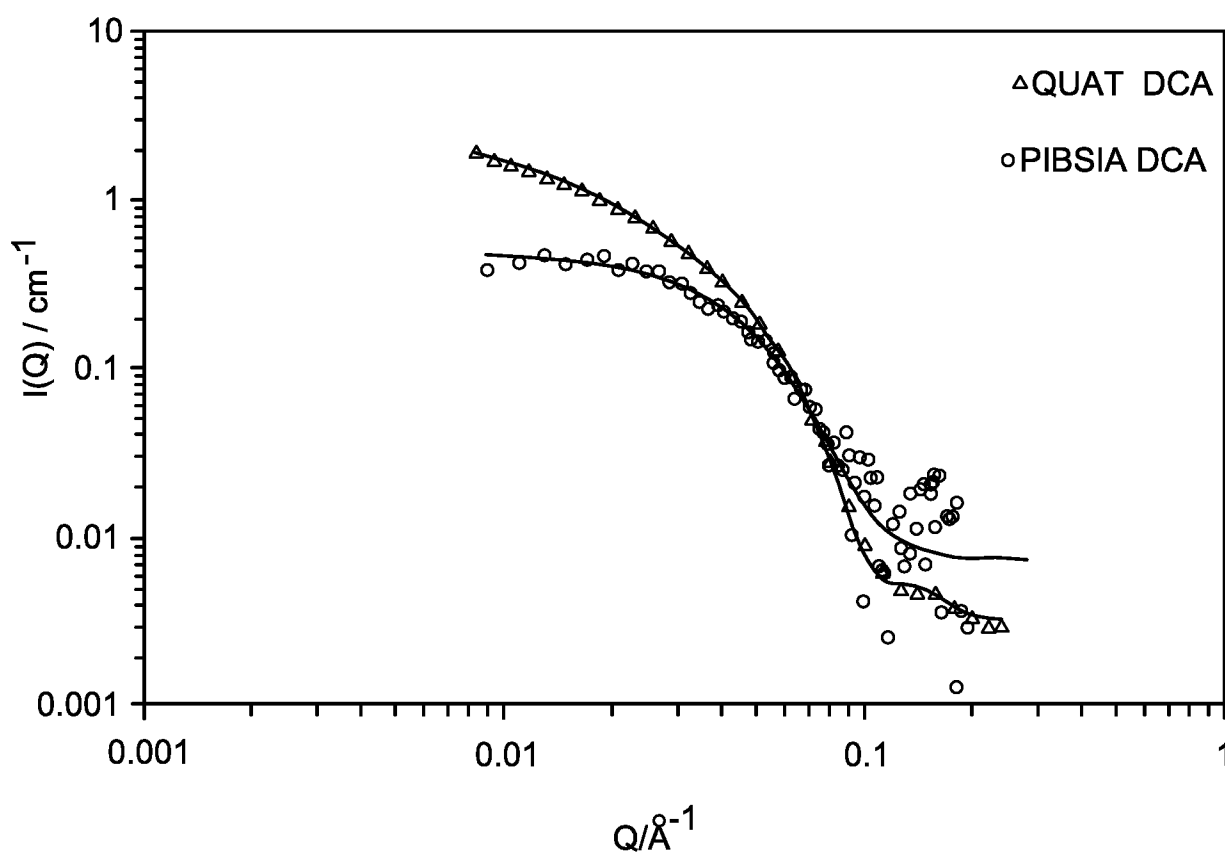


FIG. 2

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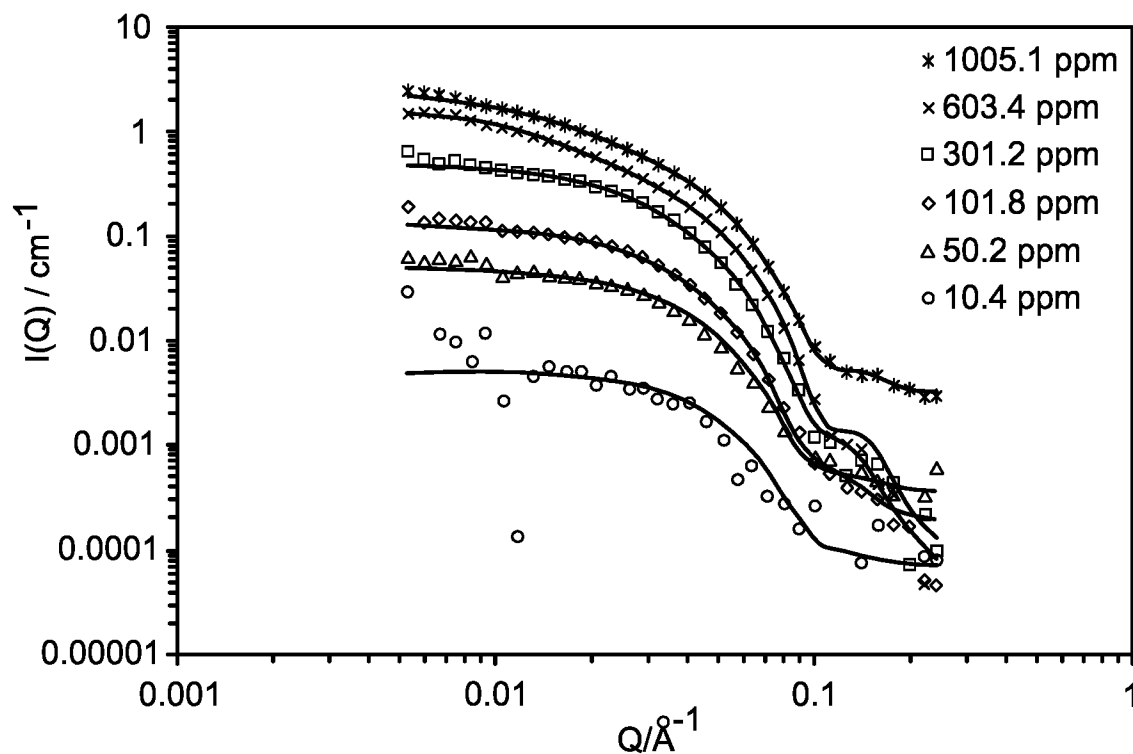


FIG. 3

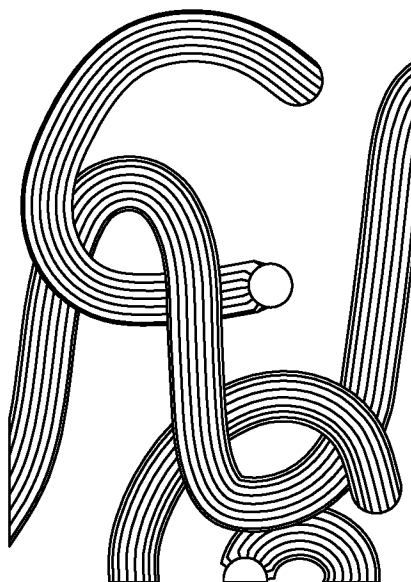


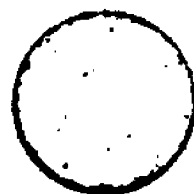
FIG. 4

FIG. 5A



PIBSI Base

FIG. 5B



Power Gain-Base

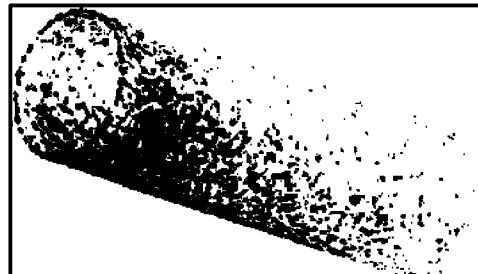
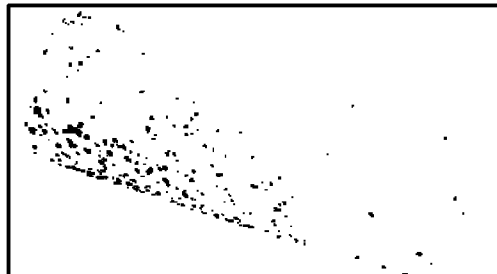


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/034728**A. CLASSIFICATION OF SUBJECT MATTER****C10L 1/12(2006.01)i, C10L 1/224(2006.01)i, C10L 1/19(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L 1/12; E21B 47/10; E21B 47/06; C10L 1/224; C09K 8/52; C10L 1/19

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: fuel, gasoline, diesel, hydrocarbon, injector, deposit control additive, DCA, detergent, surfactant, micelle, elliptical, ellipsoidal, elongated, rod-like, worm-like, quaternary ammonium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015-0096528 A1 (AFTON CHEMICAL CORPORATION) 09 April 2015 See paragraphs [0004]–[0006]; and claims 1–6.	1–3
Y	US 2011-0143972 A1 (DE CAMPO, FLORYAN et al.) 16 June 2011 See paragraphs [0007]–[0017].	1–3
A	LACEY, PAUL et al., "Fuel quality and diesel injector deposits," SAE International Journal of Fuels and Lubricants, 2012, Vol. 5, No. 3, pages 1187–1198 See the entire document.	1–3
A	CHU, ZONGLIN et al., "Wormlike micelles and solution properties of a C22-tailed amidosulfobetaine surfactant," Langmuir, 2010, Vol. 26, No. 11, pages 7783–7791 See the entire document.	1–3
A	US 2009-0235730 A1 (ALAPATI, RAMA R.) 24 September 2009 See the entire document.	1–3



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 August 2017 (28.08.2017)

Date of mailing of the international search report

28 August 2017 (28.08.2017)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

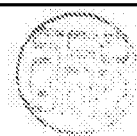


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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/034728**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 5, 6, 9, 10, 12, 13
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 5, 6, 9, 10, 12 and 13 refer to one of claims which are not drafted in accordance with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 4, 7, 8, 11, 14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/034728

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015-0096528 A1	09/04/2015	CN 104513686 A EP 2862917 A1 US 9464252 B2	15/04/2015 22/04/2015 11/10/2016
US 2011-0143972 A1	16/06/2011	EP 2092038 A2 US 2009-0163389 A1 US 7915204 B2 US 8003575 B2 WO 2008-073233 A2 WO 2008-073233 A3	26/08/2009 25/06/2009 29/03/2011 23/08/2011 19/06/2008 07/08/2008
US 2009-0235730 A1	24/09/2009	None	