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(54) Titre : LIQUIDES IONIQUES ET LEURS PROCEDES D'UTILISATION
(54) Title: IONIC LIQUIDS AND METHODS OF USING SAME

(57) **Abrégé/Abstract:**

Ionic liquid containing compositions may be used in the production, recovery and refining of oil and gas. In addition, they may be used to treat wastewater and/or to inhibit and/or prevent fouling of contaminants onto surfaces.

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(54) **Title:** IONIC LIQUIDS AND METHODS OF USING SAME

(57) **Abstract:** Ionic liquid containing compositions may be used in the production, recovery and refining of oil and gas. In addition, they may be used to treat wastewater and/or to inhibit and/or prevent fouling of contaminants onto surfaces.

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IONIC LIQUIDS AND METHODS OF USING SAME

This application claims the benefit of U.S. application serial no. 62/696,544 filed on July 11, 2018 which is herein incorporated by reference.

SPECIFICATION

Field of the Disclosure

[001] The disclosure relates to ionic liquids and methods of using ionic liquids in the production and treatment of hydrocarbon streams containing or in contact with undesirable materials.

Background of the Disclosure

[002] During the production and refining of hydrocarbon fluids produced from oil and gas reservoirs, contaminants and other undesirable materials must be removed or reduced in order for the fluids to be used for their intended purpose.

[003] At the time of production, petroleum crude is characterized by complex mixtures of different hydrocarbons (typically containing from 1 to 80 carbon atoms) differing in appearance and ranging in consistency from water to tar-like solids. Petroleum crude typically contains varying amounts of asphaltenes as well as sulfur, nitrogen, oxygen, metals, salts and other contaminants.

[004] Asphaltene precipitates form in petroleum crude during stimulation of the reservoir when the pressure drops below the onset pressure. The high viscosity of heavy crude is due, at least partially, to the presence of the asphaltenes. They are known to cause deleterious effects on the extraction of

oil by blocking production routes and tubing. For instance, asphaltene precipitates are known to flocculate and form deposits in the pores of the formation penetrated by the reservoir, coat boreholes and solidify in downhole equipment. Asphaltenes are further known to adversely impact the viscoelasticity and flow behavior of petroleum crude and to cause operational and safety issues with both hydrocarbon production and processing. Wells with excessive asphaltene deposition may incur high remediation costs but, more importantly, are exposed to levels of formation damage that can greatly shorten the productive life of the well. Asphaltene inhibitors are commonly used to inhibit or prevent the formation or precipitation of asphaltenes.

[005] Some petroleum crudes contain organic acids that contribute to corrosion or fouling of refinery equipment which are difficult to separate from the processed oil. Such organic acids include naphthenic acids. Naphthenic acids, alone or in combination with other organic acids, can cause corrosion at temperatures ranging from 150°C to 400°C. Acidic crude oils are typically treated by contacting the crude with an effective amount of inhibitors such as tetraalkylammonium hydroxide, preferably tetramethylammonium hydroxide, and preferably in solid form. The treated crude has a reduced or substantial absence of acidity.

[006] Nitrogen is also found in lighter fractions of petroleum crude as basic compounds, and more often in heavier fractions of crude oil as non-basic compounds. Nitrogen oxides can form in process furnaces during refinery of the crude. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

[007] Petroleum crude also typically contains trace metals such as copper, vanadium, and nickel. Such metals are removed during the refining process. Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of oxides such as vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they are known to poison catalysts.

[008] In addition to trace metals, crude oil often contains water, inorganic salts, and suspended solids. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed. Typically, the crude oil and hydrocarbon streams are subjected to desalting (dehydration) to remove such contaminants. The two most common methods of desalting use hot water as an extraction agent. In chemical desalting, water and chemical surfactant (demulsifiers) are added to the petroleum crude or hydrocarbon streams, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they settle out. Such contaminants may further be removed by electrical desalting, i.e., the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. A third and less-common process involves filtering the heated petroleum or hydrocarbon streams using diatomaceous earth. It is then heated to between 150°F and 350°F to reduce viscosity and surface tension for easier mixing and separation of the water. These methods all require the addition of chemical inhibitor.

[009] Once brought to the surface and collected, petroleum crude is transported to refineries. Refining begins with the distillation, or fractionation, of the crude into separate hydrocarbon groups. Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes. These converted products are then subjected to various treatment and separation processes such as extraction and hydrotreating to remove undesirable constituents and improve product quality.

[0010] For instance, sulfur may be present in hydrocarbon streams during refining (as well as in petroleum crude) as sulfhydryl compounds such as hydrogen sulfide, mercaptans, sulfides, disulfides, thiophenes, or as elemental sulfur. Hydrocarbon streams which contain appreciable quantities of such sulfur components are called "sour." Those with less sulfur are called "sweet." Sour-water stripping, often referred to as sweetening processes, either remove the sulfur compounds or convert them to odorless disulfides. Such processes use chemical scavengers.

[0011] In the past, much effort has been undertaken to inhibit the formation of contaminants during the recovery of petroleum crude from underground reservoirs, to remove contaminants from petroleum crude and hydrocarbon streams during refining and to inhibit the deposition of contaminants onto conduits used in the production of petroleum crude and refining of crude into hydrocarbons. For instance, such efforts have included methods for decreasing the viscosity of heavy oil, increasing the flow of hydrocarbons from the reservoir by minimizing the precipitation of asphaltenes, removing contaminants (such as sulfur, organic acids, and heavy metals) during refining

of the crude, inhibiting fouling of contaminants onto conduits and improving flow of petroleum crude and hydrocarbon streams through such conduits. Such efforts have required expensive inhibitors and other well treatment agents. Alternatives have therefore been sought.

Summary of the Disclosure

[0012] In an embodiment, the disclosure relates to the use of an electronically neutral ionic liquid in the treatment of a stream containing a contaminant. The ionic liquid may be of the formula:



wherein A^+ is nitrogen, a nitrogen containing heterocyclic ring, phosphorus or a phosphorus containing heterocyclic ring; and

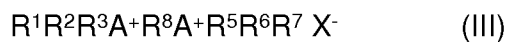
when A is or contains phosphorous or a phosphorus containing ring, X^- is an anion selected from the group consisting of halides; hydroxyl; carbonates; alkyl carbonates; bicarbonates; dithiocarbonates; trithiocarbonates; xanthates, thiocyanates; alkoxides; carboxylates; hydroxycarboxylates; sulfonates; sulfates; bisulfites; anionic amino fatty acids; anionic alkoxyated fatty acids; anionic metallic complexes, sulfur or silicon containing anions; anionic phosphate esters, anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; alkyl substituted phosphines; anionic ureas; anionic thioureas; anionic natural products; anionic thiazoles, triazoles and thiadiazoles; anionic thiols including alkylated derivatives; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers;

anionic copolymers of ethylene and vinyl acetate; anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers; anionic phosphated maleic copolymers; an anionic homo or copolymer of an oxirane or methyloxirane and mixtures thereof or a zwitterion; and

when A is or contains nitrogen, phosphorus or a heterocyclic ring thereof; X is an anion selected from the group consisting of anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; alkoxides; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof or a mixture thereof; amino fatty acids; anionic alkoxyated fatty acids; alkyl substituted phosphines; anionic urea; anionic thiourea; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers, anionic copolymers of ethylene and vinyl acetate, phosphated maleic copolymers and mixture thereof or a zwitterion.

[0013] Another embodiment is drawn to the use of ionic liquids in the treatment of a stream containing unwanted materials wherein the ionic liquid is of the formulas:





wherein:

A in formula (II) is or contains nitrogen or phosphorus or a heterocyclic ring thereof and wherein each A in formula (III) is independently selected from nitrogen or phosphorus or a heterocyclic ring thereof; and

X is an anion selected from the group consisting of halides; hydroxyl; carbonates; alkyl carbonates; bicarbonates; carboxylates; hydroxycarboxylates; sulfonates; sulfates; bisulfites; thiocyanates; dithiocarbonates; dithiocarbonates; trithiocarbonates; carbamates; dithiocarbamates; trithiocarbamates; xanthates; sulfides; polysulfides; alkoxides; anionic ureas; anionic alkyl substituted phosphines; anionic amino fatty acids; anionic alkoxylated fatty acids; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic phosphated maleic copolymers; anionic metal complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic alkyl substituted phosphines; and anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates, acrylamides and acids, optionally copolymerized with one or more ethylenically unsaturated monomers; anionic copolymers of ethylene and vinyl acetate; anionic homo and copolymers of oxirane and/or methyloxirane; anionic copolymers of olefins and vinyl acetate; and mixtures thereof; and further wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently

selected from the group consisting of hydrogen; benzyl; alkylbenzyl, or oxyalkyl (including $-\text{CH}_2\text{CH}_2\text{OH}$) or $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$); a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

[0014] Another embodiment is drawn to ionic liquids of formula (III) wherein at least one A is phosphorus or a phosphorus containing ring.

[0015] Another embodiment is drawn to ionic liquids of formula (I), (II) or (III) wherein A is or contains phosphorus or a phosphorus containing ring and X is an anion selected from the group consisting of hydroxyl; bicarbonates; alkoxides; hydroxycarboxylates; silicon containing anions; anionic amino fatty acids; anionic alkoxylated fatty acids; anionic thiophosphonate esters; alkyl substituted phosphines; anionic ureas; anionic thioureas; anionic natural products; anionic phenols; anionic phenol resins; alkoxides; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers; phosphated maleic copolymers; an anionic homo or copolymer of an oxirane or methyloxirane and mixtures thereof.

[0016] Another embodiment is drawn to ionic liquids of formula (I), (II) or (III) wherein A is or contains nitrogen or a nitrogen heterocyclic ring and the anion X is selected from the group consisting of anionic silicon containing anions; anionic thiophosphonate esters; anionic natural products; anionic phenol resins; alkoxides; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof or a mixture thereof; amino fatty acids; anionic alkoxylated fatty acids; alkyl substituted phosphines; anionic ureas; anionic thioureas; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers containing acrylamide units; anionic phosphated maleic copolymers; anionic oxirane or methyloxirane homo or copolymers; and mixtures thereof.

[0017] Another embodiment of the disclosure is drawn to ionic liquids of formula (II) or (III) wherein A in formula (II) is nitrogen and each A in formula (III) is nitrogen as defined herein and wherein X is an anion selected from the group consisting of anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic oxirane or methyloxirane homo or copolymers; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof amino fatty acids; anionic alkoxylated fatty acids; alkyl substituted phosphines; anionic ureas; anionic thioureas; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers containing acrylamide units;

phosphated maleic copolymers and mixtures thereof; and further wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are independently selected from the group hydrogen; benzyl; alkylbenzyl, or oxyalkyl (including -CH₂CH₂OH) or -CH₂CH(CH₃)OH; a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R⁸ is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and R⁸ is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene; and further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

[0018] In an embodiment of the disclosure, the ionic liquid of formulas (I), (II) and (III)) may be used:

(A) to treat a fluid produced from a subterranean formation penetrated by a reservoir;

(B) in a fluid introduced or pumped into a subterranean formation penetrated by a reservoir;

(C) in a conduit or vessel in contact with a hydrocarbon fluid, including a conduit or vessel in a refinery, treatment facility, underground reservoir extending from or to an underground reservoir;

(D) to treat a fluid processed or being processed in a refinery;

(E) to treat wastewater; or

(F) to treat a hydrocarbon fluid

[0019] In an embodiment is provided a method of using any of the ionic liquids of formula (I), (II) or (III) is provided for:

- (a) removing metals, amines and/or phosphorus compounds from a fluid stream;
- (b) reducing the viscosity of a fluid stream;
- (c) removing organic acids or inorganic salts from a fluid stream;
- (d) reducing concentration of naphthenic acid content in a fluid stream;
- (e) inhibiting or preventing fouling of contaminants onto a conduit or vessel in contact with a fluid stream or in a reservoir or refinery in which a hydrocarbon fluid is produced or processed;
- (f) inhibiting the formation or deposition of contaminants within a refinery, in a reservoir, during transport of a fluid stream or during storage of a fluid stream; and/or
- (g) clarifying wastewater or a hydrocarbon stream.

[0020] In an embodiment, a method of inhibiting or preventing the formation or precipitation of asphaltenes in a fluid stream or removing sulfur containing compounds in a fluid stream is provided with ionic liquids of formula (II) or (III) wherein X is an anion selected from the group consisting of anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof amino fatty acids; anionic alkoxylated fatty acids; alkyl substituted phosphines; anionic ureas; anionic thioureas; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic

homopolymers, copolymers and terpolymers containing acrylamide units; phosphated maleic copolymers and mixtures thereof.

[0021] In another embodiment, a method of enhancing the performance of a treatment agent as defined herein is disclosed, by contacting the treatment agent with an ionic liquid. In these instances, the ionic liquid may act as a promoter for the treatment agent, the treatment agent being a non-ionic liquid.

[0022] Another embodiment of the disclosure relates to a petroleum hydrocarbon fluid containing one or more ionic liquids of formula (I), (II) or (III).

[0023] Another embodiment of the disclosure relates to a method of treating a petroleum hydrocarbon fluid by contacting the petroleum hydrocarbon fluid with one or more of the ionic liquids of formula (I), (II) or (III).

[0024] Another embodiment of the disclosure is drawn to a method of enhancing the productivity of a hydrocarbon fluid from a subterranean formation penetrated by a well by introducing into the well any of the ionic liquids of formula (I), (II) or (III).

[0025] In another embodiment, a method of improving the stability of a petroleum hydrocarbon fluid during transport is provided wherein the petroleum hydrocarbon fluid is contacted with any of the ionic liquids of formula (I), (II) or (III).

Detailed Description of the Preferred Embodiments

[0026] The description provides specific details, such as material types, compositions, and processing conditions in order to provide a thorough description of embodiments of the disclosure. Characteristics and advantages of this disclosure and additional features and benefits will be readily apparent

to those skilled in the art upon consideration of the following detailed description of exemplary embodiments. The description herein, being of exemplary embodiments, is not intended to limit the scope of the claims.

[0027] As used herein and throughout various portions (and headings) of this patent application, the terms "disclosure", "present disclosure" and variations thereof are not intended to mean every possible embodiment encompassed by this disclosure or any particular embodiment(s). Thus, the subject matter of each such reference should not be considered as necessary for, or part of, every embodiment hereof or of any particular embodiment(s) merely because of such reference.

[0028] Certain terms are used herein and in the appended embodiments to refer to particular components. As one skilled in the art will appreciate, different persons may refer to a component by different names. This document does not intend to distinguish between components that differ in name but not function. Also, the terms "including" and "comprising" are used herein and in the appended embodiments in an open-ended fashion, and thus should be interpreted to mean "including, but not limited to" Further, reference herein and in the appended embodiments to components and aspects in a singular tense does not limit the present disclosure or appended embodiments to only one such component or aspect, but should be interpreted generally to mean one or more, as may be suitable and desirable in each particular instance. Thus, the use of the terms "a", "an", "the" the suffix "(s)" and similar references are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

[0029] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. Unless stated otherwise, any range of values within the endpoints is encompassed. For example, where the endpoints of a range are stated to be from 1 to 10, any range of values, such as from 2 to 6 or from 3 to 5 will be defined by the range.

[0030] All references are incorporated herein by reference.

[0031] The phrase “ionic liquid” refers to neutral molten salts composed entirely of ions and which are liquid at ambient or near ambient temperatures. The phrase shall include those quaternary organic salts of the formula (I), (II), (III), (IV) or (V) as described herein. The ionic liquid may function as an inhibitor.

[0032] The phrase “treatment agent” shall refer to any material, other than an ionic liquid, which enhances the performance of an ionic liquid.

[0033] The phrase “treatment composition” shall refer to a composition resulting from contact of an ionic liquid with a treatment agent. The phrase shall include blends, mixtures, complexes and reactions products of the ionic liquid and treatment agent.

[0034] As used herein, unless otherwise restricted, “inhibit”, “inhibiting” or “inhibition” shall include (i) inhibition, prevention or reduction of the formation, agglomeration, removal and/or accumulation of contaminant deposits or other undesirable materials; (ii) inhibition, prevention, reduction, precipitation and/or deposition of contaminants; prevention of increased concentration of contaminants or other undesirable materials in a fluid; (iii) inhibit precipitation, removal or dispersal of a component from a produced fluid; the precipitation,

removal or dispersal of which could cause a reduction in the fluidity of the fluid, difficulty in transport of the fluid and/or plugging of flow lines or other channels; as well as (iv) inhibition, prevention or reduction of the removal, decay or deterioration of a metal from a surface of a conduit or vessel. The term “inhibitor” shall refer to a treatment agent capable of performing an inhibition.

[0035] As used herein, “petroleum hydrocarbon fluid” shall include crude oil, shale oil, shale gas condensate, bitumen, diluted bitumen (dil-bit), refinery fractions including distillates including gas oil cuts, finished fuel including diesel fuel, petroleum fuel and biofuel, finished petroleum products, residual oil, fuel gas, flare gas, propane, butane, liquefied petroleum gas (LPG), natural gas liquid (NGL) and combinations thereof. The ionic liquids and treatment compositions described herein are especially useful in the treatment of crude oil, bitumen, diesel fuel, petroleum fuel, biofuel, residual oil, fuel gas, flare gas, propane, butane, liquefied petroleum gas (LPG), natural gas liquid (NGL) and refinery fractions (including gas oils and light lubricating oils) and combinations thereof. In addition, any of these may contain water, brines, gases such as hydrocarbon gases, or a combination thereof.

[0036] As used herein, the word “conduit” may refer to any pipeline, pipe, tubing, tubular, flow conduit, thoroughfare or other artery in which a chemical, including a petroleum hydrocarbon fluid, travels or contacts. The word “vessel” shall include any equipment or container in which a petroleum hydrocarbon fluid is in contact, such as heat exchangers, etc. The conduit may, but not limited to, those composed of a metal, plastic or glass. The site of the “conduit” or “vessel” shall include, but not be restricted to reservoirs,

wells, pipelines, refineries, fluid processing or treatment facilities (including those where gas or oil production or treatment occur, chemical plants, thermal power stations, power plants, steel mills, natural gas processing plants, food processing plants, semi-conductor plants and HVAC systems) as well as thoroughfares leading to or from any of the above.

[0037] The ionic liquids and treatment compositions described herein may be used during the production of crude oil and gas.

[0038] In addition, the ionic liquids and treatment compositions may be used during the recovery of petroleum hydrocarbon fluids from underground reservoirs.

[0039] The ionic liquids and treatment compositions are most useful during the production of oil and gas from a well and during in a refinery operation including light-ends recovery, solid waste and wastewater treatment, process-water treatment, cooling, storage, and handling, product movement, hydrogen production, acid and tail-gas treatment and sulfur recovery.

[0040] The ionic liquids and treatment compositions may also be used during the purification or another treatment phase of an industrial product. For instance, the ionic liquids and treatment compositions may be used to treat wastewater streams. Such streams include produced water (aqueous fluids produced along with crude oil and natural gas during from reservoirs water naturally present in oil and gas bearing geological formations, aqueous fluids produced or used during the production of oil and gas from reservoirs or an industrial product, aqueous fluids produced during the refining of oil and gas or an industrial product, aqueous fluids used during the refining of oil and gas or an industrial product, aqueous fluids used or produced during transit or

storage of petroleum hydrocarbon fluids or an industrial product). Exemplary wastewater streams include flowback water, degassed sour water, boiler blowdown streams, cooling tower bleed-off/blowdown (originating from oil refineries, petrochemical and natural gas processing plants, other chemical plants, thermal power stations, power plants, steel mills, food processing plants, semi-conductor plants and HVAC systems). Wastewater streams from industrial applications include municipal wastewater treatment facilities, streams in transit to or from municipal wastewater treatment facilities, tanning facilities, and the like. Exemplary products removed during wastewater treatments described herein may include inorganic salts, polymers, breakers, friction reducers, lubricants, acids and caustics, bactericides, defoamers, emulsifiers, filtrate reducers, shale control inhibitors, phosphorus ions, ions of calcium, magnesium and carbonates, bacteria as well other production chemicals.

[0041] The ionic liquids and treatment compositions may also be used within a conduit or vessel or introduced into a conduit or vessel. The ionic liquids and treatment compositions may also be used during transit of petroleum hydrocarbon fluids or an industrial product as well as during storage of petroleum hydrocarbon fluid or an industrial product.

[0042] The ionic liquid and treatment compositions are typically liquid at relatively low temperature. While the ionic liquids are salts, they typically exhibit high flash points, good solvency for other chemicals and strong basicity.

[0043] The ionic liquid and treatment compositions may be added neat or diluted with water or solvent and/or may be formulated or blended with other

suitable materials or additives. Suitable solvents may include water, a mono or polyhydric alcohol having 1 to 8 carbon atoms or an aromatic solvent such as methanol, 2-ethylhexyl alcohol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, toluene, xylenes and combinations thereof. The amount of the ionic liquid or treatment composition in the solvent may range from about 10 vol % to about 99 vol %; alternatively from about 20 vol % independently to about 50 vol %.

[0044] Suitable ionic liquids include those of formulas (I), (II), (III), (IV) and (V). Formulas (IV) and (V) correspond to (II) and (III) wherein X is further defined and may be presented as:



wherein X is an anion selected from the group consisting of anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof amino fatty acids; anionic alkoxylated fatty acids; anionic alkyl substituted phosphines; anionic urea; anionic thiourea; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers containing acrylamide units; phosphated maleic copolymers; anionic homo or copolymers of oxirane and/or methyl oxirane; and mixtures and further wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from the group consisting of hydrogen;

benzyl; alkylbenzyl, or oxyalkyl (including $-\text{CH}_2\text{CH}_2\text{OH}$) or $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$); a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

[0045] Preferred cations include those of formula (III) having structures $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+$; $\text{R}^1\text{R}^2\text{R}^3\text{N}^+\text{R}^8\text{N}^+\text{R}^5\text{R}^6\text{R}^7$; $\text{S}^+\text{R}^1\text{R}^2\text{R}^3$; $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{P}^+$; and $\text{R}^1\text{R}^2\text{R}^3\text{N}^+\text{R}^4\text{P}^+\text{R}^5\text{R}^6\text{R}^7$.

[0046] In an embodiment, at least one A of the ionic liquids of formula (III) is phosphorus or a phosphorus containing ring.

[0047] In a preferred embodiment of formula (II) and (III), R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from the group consisting of a straight or branched C_{1-30} alkyl group, a C_{7-30} alkylbenzyl group, a C_{7-30} arylalkyl group, a straight or branched C_{3-30} alkenyl group, a C_{1-30} hydroxyalkyl group, a C_{7-30} hydroxyalkylbenzyl group, a zwitterion (such as those from oxyalkylation of an amine with an alkylene oxide; or a polyoxyalkylene group; and R^8 is a straight or branched C_{1-30} alkylene, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus ring; and the anion comprises halides, hydroxide, bicarbonate, carbonate, alkyl carbonates, alkoxides, carboxylates, or a combination thereof; and further wherein X^- is hydroxide, bicarbonate, carbonate, alkyl carbonates, alkoxides, carboxylates, or a combination thereof.

[0048] In another preferred embodiment, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 of (II), (III), (IV) and (V) are independently -H or a C_{1-20} alkyl; wherein at least one (or at least two) of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 is a C_{2-20} alkyl, preferably a C_{6-12} alkyl.

[0049] In some cases, the anion is preferably a hydroxide, bicarbonate, carbonate, alkyl carbonate or an alkoxide.

[0050] Exemplary ionic liquids of formulas (IV) and (V) include, but are not limited to, dicocodimethyl ammonium hydroxide, ditallowdimethyl ammonium hydroxide, tributylmethylammonium methyl carbonate, tetraethylammonium bicarbonate, tetrabutylammonium hydroxide, tallowtrimethyl ammonium hydroxide, cocotrimethyl ammonium hydroxide, hydrogenated tallow trimethyl ammonium hydroxide, dihydrogenated tallow dimethyl ammonium hydroxide, oxydiethylene bis(cocodimethylammonium hydroxide), or a combination comprising at least one of the foregoing. Dicocodimethyl ammonium hydroxide, ditallowdimethyl ammonium hydroxide are specifically mentioned. (As used herein, oxydiethylene bis(cocodimethylammonium hydroxide) refers to an ionic liquid having a structure represented by the formula: $\text{Coco}(\text{CH}_3)_2\text{N}^+(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_2\text{Coco}(\text{OH}^-)_2$). In an embodiment, ionic liquids having a cation of dicocodimethyl ammonium and ditallowdimethyl ammonium are preferred.

[0051] In some instances, the cation of (III) may be a polyamine, meaning the cation may have two or more nitrogen atoms (and in some cases up to 5 nitrogen atoms). In some instances, one or more of the nitrogens of the polyamine may be cationic such that the cation of (III) may be a polyamine containing two or more cationic sites (and in some cases up to 5 cationic

sites). In such cases, R^8 may correspond to $(-NR^1R^2)_y$ or $(-NR^1R^2R^3)_y$ wherein y corresponds to 1, 2 or 3 to render the number of nitrogen sites and R^1 , R^2 , and R^3 are as defined above. Specifically, y is 1 when A is a triamine, y is 2 when A is a tetraamine and y is 3 when A is a pentaamine. Exemplary are cations of diethylenediamine, triethylenetetraamine, tetraethylenepentamine and (bis) hexamethylenetriamine. In other instances, where both of A are phosphorus in (III), the cation may consist of multiple cationic sites on the phosphorus wherein R^8 may correspond to $(-PR^1R^2)_y$ or $(-PR^1R^2R^3)_y$ wherein y corresponds to 1, 2 or 3 to render the number of phosphorus sites and R^1 , R^2 , and R^3 are as defined above.

[0052] As used herein, the term “alkyl” refers to a straight or branched chain, saturated monovalent hydrocarbon group regardless whether straight or branched chain is specifically mentioned or not; “aryl” refers to an aromatic monovalent group containing only carbon in the aromatic ring or rings; “arylalkyl” refers to an alkyl group that has been substituted with an aryl group, with benzyl being an exemplary arylalkyl group; “alkylbenzyl” refers to a benzyl group that has been substituted with an alkyl group in the aromatic ring; “hydroxyalkyl” refers to an alkyl group that has been substituted with a hydroxyl group with 2-hydroxyethyl as an exemplary hydroxyalkyl group; “hydroxyalkylbenzyl” refers to a benzyl group that has been substituted with a hydroxyalkyl group as defined herein in the aromatic ring; “alkylene” refers to a straight or branched chain, saturated, divalent hydrocarbon group, and “alkenyl” refers to a straight or branched chain monovalent hydrocarbon group having at least two carbons joined by a carbon-carbon double bond. The term “substituted” as used herein means that at least one hydrogen on the

designated atom or group is replaced with another group, provided that the designated atom's normal valence is not exceeded. Substituted with a group means substituted with one or more groups.

[0053] Suitable nitrogen containing heterocyclic rings referenced herein include pyridinium, imidazolinium and a pyrrole cation (including alkylated derivatives thereof). Further reference to "nitrogen" shall include nitrogen containing cations such as an oxyalkylated nitrogen.

[0054] In an embodiment, the cation of (I), (II) or (III) is a quaternary amine salt, triethanolamine methyl chloride including polymers thereof, oxyalkylated amine, polyamine, oxyalkylated polyimines, cationic melamine acid colloid or an oxyamine such as those of the formula $(\text{CH}_3)_2\text{N}(\text{CH}_2)_x\text{OH}$ where x is 1 to 6, preferably 2.

[0055] As used herein, a polyoxyalkylene group has a formula



[0056] An alkylene polyoxyalkylene group has a formula



occurrence of R³ is independently a C₁₋₁₀ alkylene or C₂₋₆ alkylene, specifically ethylene, propylene, butylene, or a combination thereof, and y is an integer from 1 to 500, such as 2 to 30, 4 to 25, or 8 to 25.

[0057] An alkylene oxyalkylene group has a formula of -R⁷-O-R⁸-, wherein

R^7 and R^8 are each independently a C_{1-20} , or C_{1-10} , or C_{1-5} branched or straight chain alkylene. Optionally, R^7 and R^8 can be ethylene.

[0058] Exemplary halides for the anion X^- are $-Cl$, $-Br$, $-F$ and $-I$. In an embodiment $-Cl$ is preferred.

[0059] Suitable sulfur and phosphorus containing anions include sulfates

(SO_4^-), bisulfate (HSO_4^-), thiocyanate (SCN^-), thiocarbonate ($^-\overset{\overset{S}{\parallel}}{SCS^-}$),

dithiocarbamates ($^-\overset{\overset{S}{\parallel}}{R_1R_2NCS^-}$) wherein R_1 and R_2 are independently selected

from C_{1-20} alkyl groups, xanthates ($^-\overset{\overset{S}{\parallel}}{ROCS^-}$) wherein R is a C_{1-20} alkyl, sulfides (RS^-) wherein R is a C_{1-20} alkyl, anionic polysulfides ($RS(S)_xS^-$) wherein R is a C_{1-20} alkyl and x is one to five, anionic phosphate esters [$ROP(=O)(OH)_2$] and anionic phosphonate ester [$R-P(=O)(OH)_2$] (wherein R is a C_{1-20} alkyl or a C_{1-20}

oxyalkyl- (RO^-); anionic thiophosphate esters ($^-\overset{\overset{O}{\parallel}}{RP}S^-$ $^-\overset{\overset{S}{\parallel}}{R_1R_2P}-S^-$) as well as

anionic thiophosphonate esters (wherein R is a C_{1-20} alkyl or a C_{1-20} oxyalkyl- (RO^-); sulfonates ($^-\overset{\overset{O}{\parallel}}{RSO_3^-}$) wherein R is C_{1-20} alkyl or aryl or alkylaryl group; and anionic thiols (RSH) where R is $-(CH)_xH$ and x is from 1 to 4.

[0060] Exemplary oxirane or methyloxirane homo or copolymers include those containing units of the structure $-(CH_2CH_2O)_xCH_2CH(CH_3O)_y$ where x and y are independently selected from 1 to 1500.

[0061] Exemplary anionic metal complexes in formulae (I), (II) and (III) may include, but not be limited to Fe (such as Fe containing anions like $FeCl_4^-$), aluminum (such as Al containing anions like $AlCl_4^-$), etc. Further, the anionic

metal complex may be formed from copper, zinc, boron, tin and mixtures thereof.

[0062] The anion may further be an anionic natural product like anions of a polysaccharide, polyphenol or lignin. Suitable anions of polysaccharides include anionic starches (such as mixtures of amylose and amylopectin), anionic polyphenols (such as anionic flavonoids or anionic natural polyphenols and anionic tannins (such as water soluble anionic polyphenols with a molecular weight between 500 and 3,000).

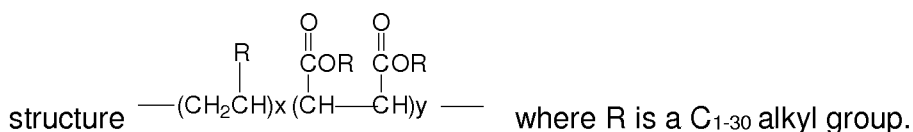
[0063] Suitable anions may also be anionic phenolics such as anionic phenols, anionic alkyl substituted phenols, anionic phenol oxyalkylates, anionic alkyl substituted phenol oxyalkylates, anionic phenolic or alkylphenol resins and anionic phenol resin oxyalkylates. Typically, the alkyl groups of the anionic phenolics are C₁₋₂₈.

[0064] The anion may also be an alkoxide. Suitable alkoxides include those of the formula RO⁻ where R is a C₁₋₃₀ alkyl or cycloalkyl group. In an embodiment, R is C₁₋₁₈ alkyl, C₆₋₁₂ aryl, or C₅₋₁₂ cycloalkyl. Exemplary alkoxides are tert-butoxide, n-butoxide, isopropoxide, n-propoxide, isobutoxide, ethoxide, methoxide, n-pentoxide, isopentoxide, 2-ethylhexoxide, 2-propylheptoxide, nonoxide, octoxide, decoxide and isomers thereof. Preferably, the alkoxides are tert-butoxide, isopropoxide, ethoxide, or methoxide. Tert-butoxide and methoxide are specifically mentioned. The alkoxides may further be anionic ethylene or propylene oxide homopolymers, anionic copolymers or terpolymers (which may optionally be crosslinked). Suitable crosslinking agents include bisphenol A or maleic anhydride.

[0065] Suitable alkyl carbonates are those of the formula ROCO_2^- , where R is a halogenated or non-halogenated linear or branched alkyl, or hydroxyl alkyl group, preferably a halogenated or non-halogenated linear or branched C_{1-8} or C_{1-5} alkyl group.

[0066] Exemplary carboxylates include formate, acetate, propionate, benzoate, n-butyrate, isobutyrate, and pivalate. Exemplary hydroxycarboxylates include octanoate, laurate, glycolate, lactate, citrate, glucarate and gluconate as well as C_{18} fatty acids such as oleate, linolate and stearate.

[0067] Suitable anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides (and derivatives thereof) include those of the general



[0068] Suitable anionic alkyl carbonates, carboxylates, anionic metal complexes, anionic natural products, anionic phenolics, alkoxides, anionic alpha olefin/maleic anhydride polymers, anionic polymers of acrylates, methacrylates and acrylamides and nitrogen and sulfur cations are those referenced in the paragraphs above.

[0069] The ionic liquids of (I), (II), (III), (IV) and (V) are salts having a melting point range of -100°C to 200°C , typically below 100°C . They are generally non-volatile and exhibit low vapor pressures and are environmentally more benign than other organic solvents, such as volatile aromatics and alkanes. They are thermally stable over a wide temperature range with some having a liquid range of up to 300°C or higher. Typically they are molten salts of organic compounds or eutectic mixtures of organic

and inorganic salts. Stability and other fundamental physical properties of the ionic liquids are influenced by the selection of cation while the selection of anion generally determines the functionality of the ionic liquid.

[0070] The ionic liquids disclosed herein may be prepared by first forming a quaternary salt followed by ion exchange with an acid or salt or by an anionic metathesis reaction with an appropriate anion source to introduce the desired counter anion. As an example, a nitrogen or phosphorus containing heterocyclic compound (such as an imidazole or pyridine) may first react with an alkylating agent to form the quaternary salt. The alkylating agent may be an alkyl chloride providing a broad range of alkyl groups on the nitrogen including straight and branched or cyclic C₁-C₂₀ alkyl groups. The quaternary salt may then be subjected to ion exchange with an acid or salt to form the ionic liquid. Typically, no other work-up is required. Any water formed in the reaction may be removed by distillation, if desired.

[0071] Ionic liquids (I), (II), (III), (IV) and (V) tailored by varying the cation and anion pairing may be combined with a treatment agent to form a treatment composition.

[0072] Treatment compositions formed by contacting the ionic liquid(s) and treatment agent(s) have been noted to provide synergy, e.g., asphaltene inhibition significantly improves when an asphaltene inhibitor (other than the ionic liquid) is in contact with an asphaltene inhibiting ionic liquid, scale inhibition significantly improves when a scale inhibitor (other than the ionic liquid) is in contact with a scale inhibiting ionic liquid, etc. In such instances, the ionic liquid may be viewed as a promoter for the treatment agent. In an embodiment, the anion of the ionic liquid may be the same as the conjugate

base of the treatment agent. For instance, a suitable ionic liquid may be prepared of formula (II) or (III) where the cation is nitrogen, each of R_1 , R_2 , R_3 and R_4 are hydrogen and anion A is a phosphonate. The ionic liquid functions as a scale inhibitor. A scale inhibiting treatment composition may consist of the ionic liquid and a scale inhibitor (other than an ionic liquid). The conjugate base of the treatment agent is a phosphonate, the same as the anion of the ionic liquid.

[0073] In one non-limiting example, the presence of the ionic liquid in the treatment composition increases the effectiveness of the treatment agent as well as the ionic liquid by at least 25% and sometimes 50% or higher compared to when the treatment agent or ionic liquid(s) is used by itself. As an example of the synergy, the combination of the ionic liquid and a conventional scavenger used to treat sour gas significantly increases the overall scavenging efficiency over either component used separately. In another example, the reduction in acidity of an acidic crude oil contacted with a treatment composition of ionic liquid and a treatment agent (such as tetramethylammonium hydroxide) is greater than when either the ionic liquid or the treatment agent is used by itself to treat the crude.

[0074] A treatment composition may be formed by contacting any of the ionic liquids of formula (I), (II), (III), (IV) or (V) with a treatment agent (other than the ionic liquid). The treatment composition may consist of the treatment agent and an ionic liquid wherein anion X of the ionic liquid is the counter-anion of the treatment agent are the same.

[0075] The ionic liquids and/or treatment compositions described herein may exhibit multiple functions. For example, an ionic liquid(s) or treatment

composition(s) may be effective as a TAN reducer as well as a corrosion inhibitor and/or scale inhibitor.

[0076] One or more ionic liquids and/or treatment compositions may be concurrently used.

[0077] The treatment agent is preferably a liquid material. If the inhibitor is a solid, it may be dissolved in a suitable solvent, thus making it a liquid.

[0078] Generally, the amount of ionic liquid(s) added to a fluid is about 1 ppm to about 5,000 ppm, or about 1 ppm to about 500 ppm, or about 5 ppm to about 150 ppm. This amount may correspond to the amount of ionic liquid(s) added to the fluid (when not combined with a treatment agent) as well as the amount of ionic liquid(s) added to the fluid as a component of a treatment composition.

[0079] In some instances, the treatment composition formed by contacting the ionic liquid(s) with the treatment agent(s) constitutes a blend, the blend exhibiting the stated synergy. In other instances, the synergy demonstrated by the treatment composition(s) and treatment agent(s) is noted by the formation of a complex when the ionic liquid is contacted with the treatment agent.

[0080] In other instances, contact of the ionic liquid(s) with the treatment agent(s) forms a reaction product. The synergy of the reaction product is noted in comparison to either reactant - ionic liquid(s) and treatment agent(s) - by itself. In some instances, the amount of ionic liquid in the treatment composition may be from about 3 to about 99 weight percent.

[0081] Contacting of the ionic liquid(s) and treatment agent(s) can be at a temperature of about -50°C to about 250°C, for example about -5°C to about

200°C or about 20°C to about 150°C, and a pressure of about 14.7 pounds per square inch absolute (psia) to about 40,000 psia or about 14.7 psia to about 20,000 psia.

[0082] When used in a petroleum fluid, hydrocarbon-containing fluid or hydrocarbon treatment fluid, the amount of ionic liquid(s) and/or treatment composition(s) can be determined based on the specific chemistry of the fluid to which it is added and/or the conditions, such as pressure and temperature, to which the fluid is to be exposed.

[0083] In an embodiment, the ionic liquid(s) and/or treatment composition(s) disclosed herein may be added to a petroleum hydrocarbon fluid in the form of a solution or dispersion. The ionic liquids and/or treatment compositions can be separately added to the petroleum hydrocarbon fluid. Alternatively, an ionic liquid and treatment can be combined to form the treatment composition which is then contacted with the petroleum hydrocarbon fluid.

[0084] Contacting of the ionic liquid or treatment composition with a hydrocarbon containing fluid can be during the production of the petroleum fluid, during refining of the petroleum fluid, during transport or storage of the petroleum fluid or during any period in between.

[0085] For instance, when used during production and/or recovery operations of petroleum from a reservoir, contacting of the ionic liquid(s) or treatment composition(s) with the fluid may be in the reservoir. Any known method of introducing the ionic liquid(s) or treatment composition(s) into the reservoir can be used.

[0086] In an embodiment, the ionic liquid(s) or treatment composition(s) is

introduced into a reservoir and then returned in produced fluid from the reservoir. For instance, the ionic liquid(s) or treatment composition(s) may be delivered into a reservoir by downhole squeezing wherein a slug of the ionic liquid(s) or treatment composition(s) is injected into the well (such as through the annulus) and returned with the produced fluid. Such an application may be preferred, for instance, where the ionic liquid(s) or treatment composition(s) can function as a scale inhibitor.

[0087] In another embodiment for the production of petroleum, the ionic liquid(s) and/or treatment composition(s) can be applied in a continuous or batch injection process through a capillary line, down the backside of the well annulus, through an umbilical line, or through an umbilical/capillary line combination. When contacting is conducted during storage, transportation and refining, the ionic liquid(s) and/or treatment composition(s) may be added to the petroleum fluid in a storage tank, transit vessel, conduit or vessel, processing unit, refinery stream and the like.

[0088] The ionic liquid(s) or treatment composition(s) may be contacted with a surface of a conduit or vessel at any point of contact in the conduit or vessel where the hydrocarbon stream is in contact or has been in contact. The ionic liquid(s) or treatment composition(s) may be effective in conduits or vessels having metallic as well as non-metallic surfaces. In a preferred embodiment, the conduits and/or vessels are metallic surfaces, such as high alloy steels, including chrome steels, duplex steels, stainless steels, martensitic alloy steels, ferritic alloy steels, austenitic stainless steels, precipitation-hardened stainless steels, high nickel content steels and aluminum.

[0089] The ionic liquid(s) and treatment composition(s) defined herein are further effective inhibitors during the storage and transportation of petroleum hydrocarbon fluids.

[0090] In a preferred embodiment, the ionic liquid(s) and/or treatment composition(s) is contacted with a hydrocarbon-containing stream under severe conditions of heat, pressure, agitation and/or turbulence.

[0091] The ionic liquid(s) and/or treatment composition(s) have particular applicability during the production of petroleum hydrocarbon fluids from underground reservoirs and transport of hydrocarbon fluids from reservoirs through conduits. The use of the ionic liquid(s) and/or treatment composition(s) thus enhances permeability of the reservoir and the productivity of the reservoir and well to produce hydrocarbons. Further, they reduce damage to conduits and vessels and prevent increase in production costs and improve the quantity and quality of recovered petroleum hydrocarbon fluids.

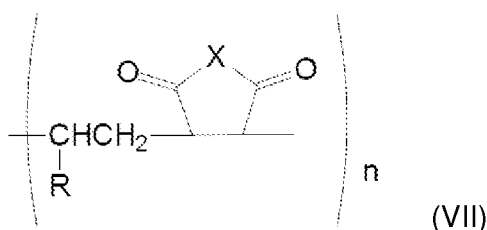
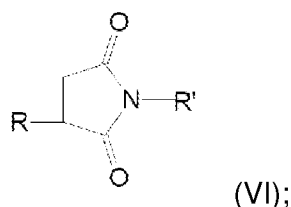
[0092] The ionic liquid(s) or treatment composition(s) also have particular applicability in the refining of petroleum hydrocarbon fluids as well as in other applications where the deposition of contaminants presents severe operation problems and quality of produced fluids.

[0093] In an embodiment, any of the ionic liquids of (I), (II), (III), (IV) and (V) may be effective in inhibiting of fouling. Alternatively, any of the ionic liquids of formula (I), (II), (III), (IV) or (V) may be combined with a treatment agent (other than the ionic liquid) to form a fouling inhibiting treatment composition. In a particular embodiment, the ionic liquid(s) and/or treatment composition(s) may be used to inhibit or prevent fouling of unwanted materials during production,

recovery and treatment of hydrocarbon streams, during in transit and storage of hydrocarbon streams as well as in other industrial operations.

[0094] Contaminants subject to fouling include scales, salts, paraffins, metals and asphaltenes.

[0095] In an embodiment, ionic liquids of formulas (I), (II), (III), (IV) and (V) may function as foulant inhibiting agents wherein anion X is the counter anion of structure (VI) or (VII).



or a mixture thereof, wherein R is a C₄ to C₁₅₀ alkyl or alkenyl (such as poly isobutyl); X is -O or NR; R' is a polyamino (such as ethylenediamine, diethylenediamine, triethylenetetraamine or tetraethylene pentamine), and n is 1 to 20.

[0096] Further, the ionic liquid of any of (I), (II), (III), (IV) or (V) may be used with a fouling inhibiting agent (other than an ionic liquid). Fouling inhibition has been noted to be greater with the synergistic combination of the ionic liquid and fouling inhibiting agent than when either the ionic liquid or the fouling inhibiting agent are used by themselves. In an embodiment, the treatment agent composition may consist of the fouling inhibitors of (VI) or (VII) with an ionic liquid having, as its anion, the counter anion of (VI) or (VII).

[0097] Any of the ionic liquid(s) of formula (I), (II), (III), (IV) or (V) referenced above may further be used as an inhibitor for scales, such as iron sulfides and mineral scales like calcium carbonate.

[0098] In an embodiment, anion X of (I), (II), (III), (IV) or (V) may be an anionic phosphate, anionic phosphate ester, anionic phosphoric acid, anionic phosphonate, anionic thiosphosphate, anionic thiosphosphonate, anionic phosphonic acid, anionic diposphonic acid, anionic phosphonate/phosphonic acid, anionic alkyl-substituted phosphine, anionic trithiocarbonate, anionic dithiocarbonate, xanthate, thiocyanate, anionic thiourea, anionic polyacrylamides, anionic methylated polyacrylamides, anionic acrylamido-methyl propane sulfonate/acrylic acid copolymer (AMPS/AA), anionic phosphinated maleic copolymer (PHOS/MA), anionic polymaleic acid/acrylic acid/acrylamido-methyl propane sulfonate terpolymer (PMA/AMPS) as well as mixtures thereof. Anionic phosphonate/phosphonic acid type scale inhibitors are often preferred in light of their effectiveness to control scales at relatively low concentration.

[0099] In an embodiment, the ionic liquid for scale inhibition is of formula (I), (II), (III), (IV) or (V) wherein the cation A is or contains nitrogen and anion X⁻ is any of the anions referenced above.

[00100] The ionic liquids described above may also be used in combination with a scale inhibitor (other than an ionic liquid). Suitable scale inhibitors include phosphates, phosphate esters, phosphoric acid, phosphonates, phosphonic acid, phosphonate/phosphonic acids, alkyl-substituted phosphonium compounds, alkyl-substituted phosphines, trithiocarbonates, dithiocarbonates, xanthates, thiocyanates, thioureas, methylated

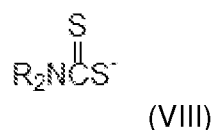
[00102] In a more preferred embodiment, the scale inhibitor is one selected from amino phosphonates, diphosphonic acids, and homopolymers or copolymers of acrylic acid. Such scale inhibitors include HEDP, homo and copolymers of acrylic acid and amino phosphonates having the structure:



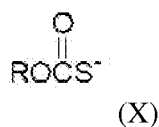
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used as the anion A of (I), (II), (III), (IV) or (V).

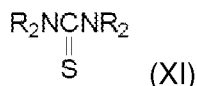
[00104] When used to treat wastewater, preferred ionic liquids include those of (I), (II), (III), (IV) or (V) wherein anion A is a trithiocarbonate, thiocyanate, dithiocarbamate such as those having the structure (VIII):



wherein R_2 is a C_1 to C_{20} alkyl or those derived from a polyamine, such as diethylenediamine, polyethyleneamines $[\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2]$ and a polyether etheramine of the general structure $\text{H}_2\text{N}(\text{CHRCH}_2\text{O})_n\text{CH}_2\text{CHRNH}_2$; a xanthate such as those having the structure (IX):



wherein R is a C_1 to C_{20} alkyl and the counter anion of a thiourea such as those having the structure (XI):



wherein each R is independently selected from a C_1 to C_{20} alkyl group.

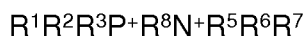
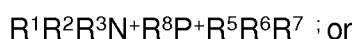
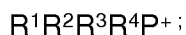
[00105] Further, a scale inhibiting treatment composition may be used to inhibit scale formation consisting of any of the ionic liquids of (I), (II), (III), (IV) or (V) (preferably an ionic liquid set forth in the preceding paragraphs) and a scale inhibitor (other than an ionic liquid) (such as a scale inhibitor set forth in the preceding paragraphs). When the ionic liquid is used with a scale inhibitor, the anion of the ionic liquid of the scale treatment composition may be the same as the counter anion of any of the scale inhibitors referenced

above.

[00106] The ionic liquid(s) or treatment composition(s) are further highly effective in the treatment of asphaltenes. While asphaltene deposition/accumulation is reduced by the use of the ionic liquids described herein, treatment composition(s) formed from asphaltene inhibitors and the ionic liquid(s) are typically more effective. The treatment compositions(s) for the treatment of asphaltenes provides a synergistic effect compared to the inhibition provided by the asphaltene inhibitor(s) or the ionic liquid(s) by themselves.

[00107] Suitable ionic liquids include those of formulas (I), (II) and (III) as defined above.

[00108] In an embodiment, the ionic liquid may be those where the cation is of the formula:



wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are as defined above. The anion of the ionic liquid may be any of those referenced above for formula (II) or (III). In an embodiment, the X^- anion is selected from halides, carbonates, alkyl carbonates, bicarbonates and carboxylates.

[00109] Exemplary ionic liquids for the treatment of asphaltenes include those of formulas (II) and (III) wherein the cation is of the formulas $R^1R^2R^3R^4P^+$; $R^1R^2R^3P^+R^8P^+R^5R^6R^7$, $R^1R^2R^3N^+R^8P^+R^5R^6R^7$ and $R^1R^2R^3P^+R^8N^+R^5R^6R^7$ and wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 represent an

anionic fatty ester homopolymer or (such as anionic fatty esters of acrylic and methacrylic acid polymers and copolymers) and anionic sorbitan monooleate, anionic phenol resins or a blend of anionic phenol aldehyde resins with amine or polyamine additives, anionic alkoxyated fatty amines and anionic fatty amine derivatives, optionally in combination with an organic metal salt.

[00110] In addition, the ionic liquid may be of formula (II) or (III) wherein the anion X is selected from anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic oxirane or methyl oxirane homo or copolymers; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof or a mixture thereof; and anionic homopolymers, copolymers and terpolymers of an ethylenically unsaturated monomer selected from the group consisting of acrylates, methacrylates, acrylamides; and further wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from the group consisting of hydrogen; benzyl; alkylbenzyl, alkylene oxyalkylene group or oxyalkyl (including -CH₂CH₂OH) or -CH₂CH(CH₃)OH); a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion.

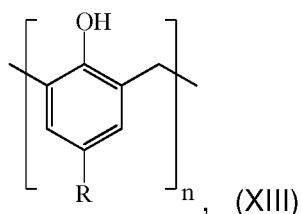
[00111] In a preferred embodiment, the anion of the ionic liquid of (I), (II) or (III) may be an anionic phenol resin such as an anionic phenol aldehyde resin or a blend of anionic phenol aldehyde resins with amine or polyamine

additives. The anionic phenol aldehyde resin may include polymers or oligomers derived from substituted-monophenols or unsubstituted-monophenols and an aldehyde. The monophenol substituents can be attached to the para, ortho, or both positions of the monophenol. Preferably the substituents are attached to the para position of the monophenol. The substituted monophenol can be an alkyl substituted monophenol. The alkyl substituents include C₁₋₂₀, C₄₋₁₈, or C₄₋₁₂ branched or linear alkyl groups. The anionic phenol aldehyde resin can be derived from a single substituted-monophenol or from combinations of two or more different substituted-monophenols or unsubstituted monophenol and an aldehyde. The molar ratio of the two or more different substituted-monophenols or unsubstituted monophenol are not particularly limited.

[00112] Exemplary anionic phenols having branched alkyl groups include anionic branched dodecyl phenol, branched nonyl phenol, tert-butylphenol, t-amyl phenol, and branched hexyl phenols such as 4-(1-methylpentyl) phenol, 4-(1,2-dimethylbutyl)phenol, and 4-(1-ethylbutyl) phenol, and 4-(1-ethyl-2-methylpropyl) phenol.

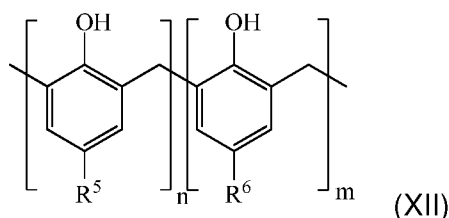
[00113] Exemplary aldehydes include formaldehyde, paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, glutaraldehyde, 1,9-nonanedial, or a combination comprising at least one of the foregoing. Formaldehyde is specifically mentioned.

[00114] In an embodiment, the anionic phenol aldehyde resin may be derived from formaldehyde and a single substituted monophenol are of the structure:



wherein R is $-H$, C_{1-20} , C_{4-18} , or C_{4-12} branched or linear alkyl groups, and n is an integer of greater than 1, typically greater than 2.

[00115] When the anionic phenol aldehyde resins are derived from two alkyl-substituted monophenols (or phenol with one alkyl-substituted monophenol) and formaldehyde, the phenol aldehyde resins can have the formula



wherein R^5 is a C_{1-20} linear or branched alkyl, R^6 is different from R^5 and is H or a linear or branched C_{1-20} alkyl, n and m are integers greater than 1. In an embodiment, R^5 is a C_{7-16} linear or branched alkyl and R^6 is a $C_{1-20, y}$ typically a C_{1-6} , linear or branched alkyl. The value of n:m can vary broadly, for example about 99:1 to about 1:99, about 1:20 to about 20:1, or about 1:10 to about 10:1. Optionally in some embodiments, the value of n:m can be about 1:5 to about 5:1. Optionally in other embodiments, the value of n:m can be about 1:2 to about 2:1.

[00116] When the ionic liquids described in the paragraphs above are combined with an asphaltene inhibitor (other than an ionic liquid), the anion of the ionic liquid may be the same anion as the counter anion of the asphaltene inhibitor

[00117] Typically, the amount of ionic liquid or asphaltene inhibiting treatment composition for the treatment of petroleum hydrocarbon fluids is about 10 ppm to about 10,000 ppm, or about 50 ppm to about 5,000 ppm, or about 100 ppm to about 1,000 ppm based on total volume of the fluid containing the ionic liquid or treatment composition.

[00118] In a preferred embodiment, the asphaltene inhibiting treatment composition(s) described herein provides greater asphaltene stabilization by reducing asphaltene deposition/accumulation (in terms of amount, tendency, and/or the rate of deposition/accumulation) than when the ionic liquid or asphaltene inhibitor is used by itself. Further, the asphaltene inhibiting treatment composition described provides greater asphaltene stabilization than conventional asphaltene inhibitors. Processing of petroleum hydrocarbon fluids is therefore improved by the ionic liquid and/or asphaltene inhibiting treatment composition(s) described herein.

[00119] The ionic liquids of formulas (I), (II), (III), (IV) and (V) may further be used to remove metals, metal salts, phosphorus and amines from hydrocarbon fluids (as well as industrial fluids)

[00120] Suitable removal agents include complexing agents such as EDTA and HEDP, glycolic acid, thioglycolic acid, gluconic acid, hydrazines, hydroxyacids, trithiocarbonates, dithiocarbamates, hydropolysulfide carbonothioylbis-disodium salt, sulfonated styrene-maleic anhydride copolymer (SSMA), copolymers of acrylic acid and sulfonated hydrophobic, aromatic monomers, poly(methacrylic acid) (PMA), poly(acrylic acid) (PAA), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), ethyl vinyl acetate polymer, and acid catalyzed nonyl phenol resin oxyalkylate.

[00121] Glycolic acid is a preferred removal agent for the removal of phosphorus since it is known to solubilize the phosphorus contaminants by forming phosphates or phosphoric acid which dissolves in the wash water.

[00122] In a preferred embodiment, the ionic liquid for removing metals, metal salts, phosphorus and amines are those of formulas (I), (II), (III), (IV) and (V) wherein the X anion is the counter anion of the removal agents set forth above.

[00123] In addition to the ionic liquids referenced above, metals, metal salts, phosphorus and amines may also be removed from hydrocarbon fluids with a treatment composition containing the ionic liquid and a removal agent. Suitable agents include those removal agents set forth in the paragraphs above.

[00124] In some instances, metals removed by the ionic liquids or treatment compositions may originate from contamination of the crude from several sources including completion and workover brines (such as those containing sodium calcium and/or zinc); formation minerals, clay, silt and sand from the wellbore; and metallic corrosion of conduits and vessels during production, storage or transport of petroleum hydrocarbon fluids.

[00125] Contaminated metals in petroleum hydrocarbon fluids include Groups IA, IIA, VB, VIIB, VII, IIB, IVA and VA of the Periodic Table. In an embodiment, the metals include calcium, iron, zinc, silicon, nickel, sodium, potassium, vanadium, mercury, manganese, barium, zinc, aluminum or copper.

[00126] The amines removed by use of the ionic liquids and treatment compositions include monoethanolamine; diethanolamine; triethanolamine; N-

methylethanolamine; N,N-dimethylethanolamine; morpholine; N-methyl morpholine; ethylenediamine; methoxypropylamine; N-ethyl morpholine; N-methyl ethanolamine, N-methyldiethanolamine and combinations thereof. Such amines may originate from nitrogen-containing compounds used to scrub hydrogen sulfide from refinery gas streams in amine units as well as amines used as neutralizers in crude unit overhead systems

[00127] Phosphorus compounds removed by the ionic liquids and treatment compositions may originate from reactive phosphorus species used or produced during stimulation of the formation penetrated by the reservoir.

[00128] Removal of metals, metal salts, phosphorus and amines from fluids is typically performed in a desalter. Desalting is necessary prior to further processing to avoid fouling. In addition to being detrimental to conduits and vessels, metals, metal salts, phosphorus and amines are detrimental in downstream processing operations of petroleum hydrocarbon fluids, including coking.

[00129] The removal of metals and/or amines and/or phosphorus from the petroleum hydrocarbon fluid (or other industrial fluid) in the desalter includes partitioning, sequestering, separating, transferring, eliminating, dividing, etc. Typically, the ionic liquid(s) or treatment composition(s) first extract metals, amines and phosphorus components from the petroleum hydrocarbon fluid in the desalter followed by wash water which forms a water-in-oil emulsion. The emulsion is resolved and the contaminants removed. Solubilized metals (such as inorganic salts like sodium and potassium) and water insoluble metal organic acid salts (such as calcium naphthenate and iron naphthenate) may

be dispersed as particulates in the oil in an emulsion and removed as wastewater.

[00130] In a two-step desalting process, the ionic liquid or treatment composition may then be mixed with the petroleum hydrocarbon fluid separated from the resolved emulsion. Fresh wash water may then be added to a second downstream desalter for resolution.

[00131] During desalting, the ionic liquid or treatment composition effectively settles the metal from the fluid. The amount of ionic liquid or treatment composition introduced to the desalter may be dependent on the nature of the hydrocarbon, the concentration of metal species, phosphorus species and/or amines to be removed as well as the temperature and pressure conditions in the desalter.

[00132] In addition to the ionic liquids referenced above, metals, metal salts, phosphorus and amines may also be removed from hydrocarbon fluids with a treatment composition containing the ionic liquid and a removal agent. Suitable agents include those removal agents set forth in the paragraphs above. Suitable removal agents include any of the complexing agents recited above in their non-anionic form. In another embodiment, ionic liquids of formulas (I), (II), (III), (IV) and (V) may be used to inhibit, prevent or reduce corrosion of metal from a surface of a conduit or vessel. Such corrosion may be caused, for example, from high salt fluids used in drilling and completion, acidic environments such as gases like carbon dioxide and hydrogen sulfide, organic solvents, etc.

[00133] The ionic liquids and treatment compositions described herein may further be used to remove or reduce sulfur compounds (such as hydrogen

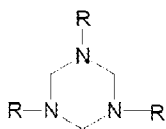
sulfide and mercaptans and, in some cases, thiophenes, disulfides and alkyl sulfides) from hydrocarbon streams.

[00134] Suitable ionic liquids for the reduction or removal of sulfur containing compounds may be those of formula (I), (II), (III), (IV) or (V) as defined above. In one preferred embodiment the ionic liquid is of formula (I), (II) or (III).

[00135] In an embodiment, the ionic liquid may be combined with a treatment agent (other than the ionic liquid) for effective removal of sulfur containing compounds in aqueous or gaseous streams. The treatment agent is hereafter referred to a “hydrogen sulfide scavenger”) which shall include compounds useful in the treatment of aqueous and hydrocarbon substrates that are rendered “sour” by the presence of mercaptans, hydrogen sulfide and other sulfhydryl compounds. The aqueous and hydrocarbon substrates include crude oil and/or produced gas; wastewater streams (such as those in transit to or from municipal wastewater treatment facilities), tanning facilities, unrefined and refined hydrocarbon products derived from petroleum or from the liquefaction of coal, including natural gas, distillates such as gasolines, distillate fuels, oils, and residual fuels and to vapors produced by the foregoing materials.

[00136] Exemplary hydrogen sulfide scavengers include maleimides, aldehydes, amines, amine aldehyde condensates, carboxamides, alkylcarboxyl-azo compounds, cumine-peroxide compounds, morpholino and amino derivatives such as diaminomethanes, imines and triazines.

[00137] In a preferred embodiment, the hydrogen sulfide scavenger may be a triazine, such as a 1,3,5 hexahydro triazine having the structure:



wherein each R is independently selected from methyl or hydroxyethyl.

[00138] Other preferred scavengers include diaminomethanes of the formula $R_2NCH_2NR_2$ wherein each R_2 is independently selected from C_1 to C_8 alkyl; imines of the formula $RN=CHR$ wherein each R is independently selected from a C_2 - C_{14} alkyl, alkenyl or oxyalkyl (such as, for example $-CH_2CH_2OH$) or an aldehyde, such as glyoxal.

[00139] In a preferred embodiment, the anion represented by X^- in formula (I), (II) or (III) is the counter anion of any of the hydrogen sulfide scavengers referenced above. For instance, anion X^- in (I), (II) or (III) may be an anionic maleimide, anionic amine, anionic amine aldehyde condensate, anionic carboxamide, anionic alkylcarboxyl-azo compounds, anionic cumine-peroxide compounds, anionic morpholino and anionic amino derivatives.

[00140] In a preferred embodiment, a treatment composition may be used in the removal of sulfur containing compounds. The treatment composition may contain the ionic liquid of formula (I), (II), (III), (IV) or (V) and any of the hydrogen sulfide scavengers referenced above. In an embodiment, the anion of the ionic liquid is the same counter anion as the hydrogen sulfide scavenger. For instance, the treatment composition may be composed of an ionic liquid of (III) wherein A is or contains nitrogen, R^1 , R^2 , R^3 and R^4 are each hydrogen and anion A is a carboxamide.

[00141] The ionic liquids and treatment compositions containing the ionic liquid and hydrogen sulfide scavenger have good solvency for sulfur compounds. Sulfur compounds may thus be removed into a hydrocarbon

solution containing the ionic liquid or composition even when the sulfur compound is not particularly acidic. For instance, contact of the ionic liquids or treatment composition containing the ionic liquid and hydrogen sulfide scavenger causes a reaction with hydrogen sulfide or low molecular weight mercaptans to render products that can then be extracted from the distillate with caustic solutions, solid absorbents or liquid absorbents. Where the method includes extraction, the extraction may be into the solution containing the ionic liquid or treatment composition itself, or the sulfur compounds may be extracted by a second treatment with additional ionic liquid or the treatment composition containing the ionic liquid and hydrogen sulfide scavenger, water, caustic, clay, etc. In an embodiment, the ionic liquids and compositions are especially active when formulated in methanol as methanol appears to make the ionic liquids and compositions an especially good solution to extract all types of sulfur compounds from the hydrocarbon stream.

[00142] It is preferred that the ionic liquid and/or the treatment composition containing the ionic liquid and hydrogen sulfide scavenger be introduced to the hydrocarbon stream as a homogeneous mixture. Where water is present, the hydrogen ionic liquid and the hydrogen sulfide scavenger are selected so that the product of the ionic liquid or composition containing the ionic liquid and the hydrogen sulfide scavenger are soluble both in water and in the feedstream. For liquid systems, suitable solvents for dissolving the ionic liquid and/or composition include polar and non-polar solvents such as water, alcohols, esters, benzene and benzene derivatives. The preferred solvents include water, ethyl acetate, acetone, kerosene, aromatic naphtha, benzene, toluene and xylene.

[00143] In general, the ionic liquid and/or treatment composition containing the ionic liquid and hydrogen sulfide scavenger is injected into or otherwise brought into intimate contact with the liquid hydrocarbon and sulfur containing compounds and, when present, water and/or solvent in any convenient manner. With emissions from a residual fuel oil, the ionic liquid and/or treatment composition may be stirred into the fuel oil. When used with a natural gas, the natural gas may be scrubbed with an aqueous or nonaqueous solution of the ionic liquid or composition containing the ionic liquid and the hydrogen sulfide scavenger. Additionally, when the natural gas contains water vapors, the ionic liquid and/or composition containing the ionic liquid and the hydrogen sulfide scavenger may be injected into a stream of the gas moving within a conduit. In such case, when the water vapors are removed from the natural gas as a liquid, the product of the ionic liquid or treatment composition will also be removed. In general, it is desirable to conduct the process in temperatures at between from about 40 to about 200°C, preferably between from about 85 to about 120 °C.

[00144] The ionic liquid or treatment composition containing the ionic liquid and the hydrogen sulfide scavenger may also be introduced into or onto an aqueous substrate for removing or reducing the sulfur containing compounds.

[00145] The amount of ionic liquid or treatment composition used will depend on the amount of the sulfur containing compounds in the medium being treated. In general, the amount of the ionic liquid or treatment composition added to the medium is at least an effective scavenging amount, for example, from about 20 ppm to about 2,000 ppm or more, preferably from

about 40 to about 1,200 ppm, and more preferably from about 100 to about 400 ppm of the sulfur containing compounds.

[00146] The ionic liquids of formula (I), (II), (III), (IV) or (V) and compositions containing the ionic liquids may further be used to reduce or remove acids (in particular carboxylic acids) from hydrocarbon fluids as well as wastewater. Such acids are typically present in petroleum crude as well. In addition, such acids are often produced during refining as they are easily distilled.

[00147] The presence of carboxylic acids in produced crude as well as in hydrocarbon refining and processing streams causes corrosion and fouling. In addition, the polarized character of the carboxyl groups promotes formation of emulsions, especially in heavier petroleum fluids. Ionic liquids of formulas (I), (II), (III), (IV) and (V) further break emulsions and/or minimize or prevent the likelihood of their formation. The demulsifying effect seen with the ionic liquids minimizes negative downstream effects including emulsions in desalters as well as impurities and decomposition products or corrosive effects.

[00148] In a preferred embodiment, the ionic liquid may be used to reduce the concentration of naphthenic acids in petroleum crude or bitumen. Naphthenic acids are also present in lighter distilled fractions including, for example, gas oil. They are composed predominately of carboxylic cycloaliphatic acids substituted with alkyl groups as well as non-cycloaliphatic acids. Aromatic, olefinic, hydroxyl and dibasic acids may also be present in minor amounts. Treatment of petroleum hydrocarbon fluids with the ionic liquid compositions renders higher quality petroleum hydrocarbon fluids which may be marketed at a higher price.

[00149] The presence of naphthenic acids contributes significantly to the acidity of crude oils and bitumen and is a major cause of corrosion and fouling in metallic conduits and vessels especially at high temperatures. Typically, petroleum hydrocarbon fluids are heated to about 175°C. to about 400°C., and more typically from about 205°C. to about 400° C. At these temperatures, naphthenic acid induced corrosion (as well as corrosion attributable to other similar organic acids or phenols such as cresylic acid) is extremely aggressive and difficult to inhibit, particularly in lighter fractions.

[00150] While the ionic liquid containing treatment composition is normally used to reduce the concentration of organic acids in petroleum crude, it may also be used to reduce the concentration of acid in a partially refined or fraction of hydrocarbon product and most notably synthetic crude oil, bitumen, shale oil, naphtha, gas oil, vacuum gas oil, deasphalted oil, demetallized oil, light coker or heavy coker gas oil, etc.

[00151] Preferred ionic liquids for the removal of acids (including naphthenic acid) are those, having as cation, trialkyl or tetraalkyl ammonium (such as tetramethylammonium, ethyltrimethyl ammonium, tetraethyl ammonium and tetrapropyl ammonium) and, as anion, members selected from hydroxide, alkoxides, carbonates, methylcarbonates and bicarbonates. Specific preferred ionic liquids include tetramethylammonium hydroxide, ethyltrimethylammonium hydroxide, choline hydroxide and (ethoxide)trimethyl ammonium.

[00152] Ionic liquids of formulas (I), (II), (III), (IV) and (V) are also effective in the removal of mineral acids such as hydrochloric acid, phosphoric acid and sulfuric acid which are often present as the oxidized form of hydrogen sulfide

in a liquid stream.

[00153] The decrease in naphthenic acid content is evident by a lower total acid number (TAN). TAN, a commonly accepted criterion for oil acidity, represents the number of milligrams of potassium hydroxide required to neutralize the acidity of 1 gram of oil. In instances, contact of the ionic liquids or inhibitor s described herein neutralizes and lowers the TAN to less than 0.5 milligrams. This is the case even with crude oils possessing high levels of naphthenic acidity (requiring between 3 to 10 mg of potassium hydroxide per gram of oil to neutralize the acidity). TAN may be determined according to ASTM D-664.

[00154] Reduction or removal of acids using ionic liquids of formulas (I), (II), (III), (IV) and (V) and treatment compositions containing the ionic liquid further provide more efficient transportation and storage of petroleum hydrocarbon fluids.

[00155] Ionic liquids of formulas (I), (II), (III), (IV) and (V) and treatment compositions find particular applicability in the reduction or removal of high molecular weight organic acids which are not easily removed by traditional methods.

[00156] In an embodiment, a preferred TAN reducing agent is formed by contacting an ionic liquid with an alkali metal (like Li, Na and K) or alkaline metal (like Mg and Ca) with a hydroxide or oxide. Potassium hydroxide is exemplary. Typically, the volume ratio of ionic liquid to alkali hydroxide is from about 95:5 to about 5:95.

[00157] In another embodiment, a preferred TAN reducing agent is an ionic liquid contacted with an amine, such as a tertiary diamine, optionally with an

alkali hydroxide. The combination of the ionic liquid and amine with caustic neutralizes naphthenic acids or breaks or prevents the formation of emulsion and reduces TAN much greater than either the ionic liquid or the tertiary amine by itself.

[00158] The ionic liquids of formulas (I), (II), (III), (IV) and (V) may be used in combination with another ionic liquid or one or more treatment agents. The treatment agent may not be restricted to those which decrease acid concentration. For instance, a TAN reducing ionic liquid may be combined with an asphaltene stabilizing ionic liquid or treatment composition as referenced above which assists in viscosity reduction of the petroleum hydrocarbon fluid (in addition to lowering the concentration of naphthenic acid). In an application, for instance, the TAN reducing ionic liquid may be combined with a mixture of ionic liquids (such as quat hydroxides) effective in stabilizing asphaltenes and improving viscosity. Suitable quat hydroxides include those of the formula $R_4^+OH^-$ where R is a C₁-C₁₈ (preferably C₁-C₆) alkyl group. Further, the TAN reducing ionic liquid or treatment composition may be combined with ionic liquids effective as demulsifiers to more efficiently separate oil and water emulsions. Alternatively, the TAN reducing ionic liquid or treatment composition may be combined with a known demulsifying agent, such as a triethanolamine ethoxylated phenol resin.

[00159] The use of the ionic liquids or treatment compositions to lower TAN may be conducted at various stages in refinery operations or upstream. For instance, the process can be implemented to treat influent feedstock in a refinery or fractions thereof. In alternative embodiments, the process can be implemented upstream of or within a gas oil separation plant, for instance,

downstream of desalting stages.

[00160] Typically, the ionic liquid and/or treatment composition and caustic are contacted at a temperature from about 50°C to about 350°C, preferably from about 100°C to about 150°C. The mixture may then be separated into an aqueous (wastewater) phase and a neutralized hydrocarbon phase. In an embodiment, the ionic liquid and/or treatment composition and caustic may be dissolved in a non-aqueous solvent, such as methanol.

[00161] In an embodiment, a petroleum hydrocarbon fluid containing naphthenic acid is contacted (optionally in the presence of a catalyst) with the alkali (additive) and TAN reducing ionic liquid for a period sufficient to neutralize at least a portion of the naphthenic acids. The time for sufficient TAN reduction is dependent on the nature of the petroleum hydrocarbon fluid to be treated, its acid content and the amount and type of ionic liquid and the amount of potassium hydroxide used. Typically, TAN reduction is for about 1 hour to about 15 hours.

[00162] The ionic liquid of formulas (I), (II), (III), (IV) and (V) and treatment composition may also be used to remove organic acids as well as inorganic salts (such as iron sulfide, barium sulfate, etc.) from wastewater. Preferred ionic liquids for the removal of inorganic salts from wastewater include phosphonic containing ionic liquids as referenced above and urea choline.

[00163] Further, the ionic liquid of formulas (I), (II), (III), (IV) and (V) may be used to clarify water, such as in the clarification of wastewater. In an embodiment, the ionic liquids may be combined with a clarifier (other than the ionic liquid). In an embodiment, the ionic liquid or treatment composition containing the ionic liquid and clarifier may be added to an aqueous system

previously subjected to flocculation for the separation of colloidal particles from the water.

[00164] Exemplary ionic liquids for water clarification include, but are not limited to, those wherein anion X^- of formula (I), (II), (III), (IV) or (V) is selected from anionic polycondensates based on N,N'-bis[3-(dimethylamino)propyl]urea, anionic polymers (including homopolymers, copolymers and terpolymers) containing acrylic acid, polyacrylate copolymers, anionic polyacrylamide homo and copolymers, anionic methylated polyacrylamide homo- and copolymers, anionic poly(acrylate/acrylamide) copolymers, anionic polycondensate based on alkanolamines, anionic dithiocarbamates, in particular anionic polycondensates based on triethanolamines, and combinations thereof.

[00165] Where a composition containing both ionic liquid and clarifier (other than a non-ionic liquid) are used to clarify water, the clarifier may be selected from polycondensates based on N,N'-bis[3-(dimethylamino)propyl]urea, acrylic acids based polymers including polyacrylate copolymers, polyacrylamide homo and copolymers, methylated polyacrylamides and copolymers and homopolymers thereof, poly(acrylate/acrylamide) copolymers, polycondensate based on alkanolamines and dithiocarbamates, In a preferred embodiment, the clarifier is a polycondensate based on triethanolamine. Mixtures of clarifiers may also be used.

[00166] The effective amount of ionic liquid and/or treatment composition containing the ionic liquid and the clarifier (other than the ionic-liquid) may range from about 0.1 ppm independently to about 50,000 ppm, alternatively from about 1 ppm independently to about 3000 ppm, or from about 5 ppm

independently to about 1000 ppm.

[00167] The ionic liquids of formula (I), (II), (III), (IV) or (V) may further be used to reduce the viscosity of a fluid. In addition, a composition of the ionic liquid and a viscosifying agent (other than the non-ionic liquid) may be used. Viscous fluids are typically required in stimulation operations to carry proppant into the well and into created or enlarged fractures. Viscosity reduction is needed after the stimulation operation is complete in order to pump fluids out of the well.

[00168] Viscosifying agents which may be used in combination with ionic liquids of formula (I), (II), (III), (IV) or (V) include redox reaction products of a fatty acid with an alkali or alkali earth metal base, unsaturated fatty acid such as olive oil, canola oil, flax oil, corn oil, soybean oil, borage oil, cod liver oil, salmon oil, nutritional oil blends, peroxides, persulfates such as sodium persulfate, ammonium persulfate, potassium persulfate, potassium peroxymonosulfate, an oxyacid or oxyanion of halogen, for instance, hypochlorous acid, a hypochlorite, chlorous acid and chlorites, chloric acid and chlorates, perchloric acid perphosphates, perborates, percarbonates and persilicates.

[00169] The ionic liquid for reducing the viscosity of the fluid may include those of formula (I), (II), (III), (IV) or (V). Preferably anion X^- is selected from anionic reaction products of a fatty acid with an alkali or alkali earth metal base, anionic unsaturated fatty acid such as olive oil, canola oil, flax oil, corn oil, soybean oil, borage oil, cod liver oil, salmon oil, anionic nutritional oil blends, anionic peroxides, anionic persulfates such as sodium persulfate, ammonium persulfate, potassium persulfate, anionic potassium

peroxymonosulfate, anionic oxyacids or oxyanion of halogen, for instance, hypochlorous acid, a hypochlorite, chlorous acid and chlorites, chloric acid and chlorates, perchloric acid perphosphates, perborates, percarbonates and persilicates.

[00170] In an embodiment, anionic X of formula (I), (II), (III), (IV) or (V) is the same as the counter anion of the water clarifier present in the treatment composition.

[00171] Examples.

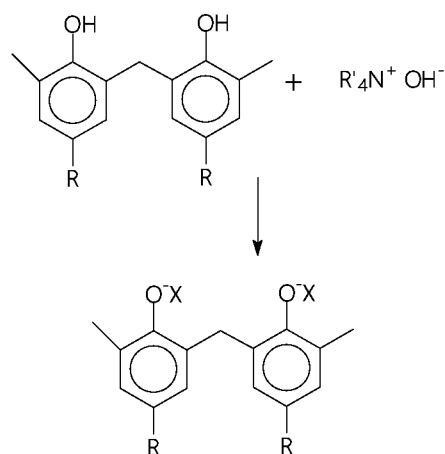
[00172] All percentages set forth in the Examples are given in terms of weight units except as may otherwise be indicated.

[00173] Example 1. Preparation of a phenol resin derivative. To a 250 ml round bottom flask fitted with a magnetic stirrer, condenser, addition funnel and a Dean-Stark trap was added 44 grams of xylene, 40 grams (0.18 mole) of p-nonyl phenol and 0.8 grams (0.002 moles) of p-dodecylbenzene sulfonic acid catalyst. The mixture was stirred and heated to 80 °C and then 14.8 grams (0.18 mole) of 37% aqueous formaldehyde was added dropwise. After complete addition of formaldehyde, the mixture was stirred for 1 hour and the temperature was then increased to distill off all water from the reaction mixture. The water distillate was collected in the Dean Stark trap and any xylene collected was returned to the reaction vessel. Heating was continued until the theoretical amount of water was collected in the trap. The sample was then cooled to room temperature.

[00174] Example 2. Preparation of ionic liquids by anion exchange. To a 20 gram sample of the resin solution prepared above in Example 1 was added dropwise 2 grams of 50% methanolic potassium hydroxide. The mixture was

stirred while heating at 60 °C for 30 minutes. About 2.9 grams of bis-(2hydroxyethyl), methyl cocoammonium chloride was then added dropwise with stirring. Heating was continued at 60 °C for another hour and then the solution was filtered while still hot to remove the potassium chloride precipitate that formed in the mixture. This procedure rendered a product with a 1:0.25 resin to quat molar ratio. To make other ratios, the amount of the potassium hydroxide solution and the quaternary ammonium chloride were scaled up accordingly while keeping the amount of resin and the reaction conditions constant.

[00175] Example 3. Preparation of ionic liquid using neutralization procedure with quaternary ammonium hydroxides. A 20 gram sample of the resin prepared above was stirred at room temperature while 4.1 grams of 55% aqueous tetrabutylammonium hydroxide was added dropwise. The mixture was stirred for 1 hour after addition of the base and the product was then used. This procedure gave a product with a 1:0.25 resin to quat molar ratio. To make other resin/quat ratios, the amount of the quaternary ammonium hydroxide was scaled up accordingly while keeping the amount of resin and the reaction conditions constant. Some of the quaternary ammonium hydroxides were diluted aqueous solutions and formed a separate aqueous layer when cooled after the 1 hour stir period. In these cases, the upper, organic phase containing the ionic liquid product was decanted away from the aqueous phase. The reaction may be summarized as follows:



X = independently H, $\text{R}'_4\text{N}^+$

R = (C_1 to C_{20} alkyl)

R' = C_1 to C_{20} alkyl, alkylaryl, ethoxyalkyl ($\text{CH}_2\text{CH}_2\text{O}-\text{R}$), propoxyalkyl $\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-\text{R}$

[00176] Example 4. Measuring the stability of asphaltenes. A test instrument was equipped with a coherent near-infrared (NIR) source that transmitted through a sample. The device also had a solid-state detection system capable of measuring the change in intensity upon titration with an asphaltene precipitant (a nonsolvent such as pentane). An inflection point could be observed in a plot of transmittance vs. the volume of added non-solvent as flocculation began. The point of inflection, expressed as the asphaltene stability index (ASI), corresponded to the point of asphaltene precipitation and provided a relative measure of the asphaltene's stability in the oil.

The following scale of ASI values was used that classifies the feedstock with respect to its stability and fouling potential:

- 0-130 ASI: High fouling potential
- 130-200 ASI: Medium fouling potential
- 200 and higher ASI: Low fouling potential.

This technique was used to measure the stability of crude, crude blends and the effects of chemical additives upon asphaltene stability.

A 0.1 ml sample of a crude oil was placed in the test instrument and heated to 70 °C. The instrument titrated the crude oil sample with heptane while measuring transmittance of a laser through the sample. When enough heptane had been added to destabilize the asphaltenes, they began to precipitate and block the path of the laser. The amount of heptane required to destabilize the asphaltenes was recorded from the maximum point on the plot of the % transmittance vs ml heptane added and reported as the ASIT value. Higher values indicate more stable asphaltenes in the crude oil as larger amounts of heptane were required to destabilize them. The results are shown in Table I.

Table I

Resin (anion)	Cation	Resin OH/cation molar ratio	Dose (ppm)	ASIT Value
Untreated crude	None	---	---	27.84
P - Nonylphenol/formaldehyde acid catalyzed resin	None	---	5000	34.18
"	Tetrabutylammonium hydroxide	1: 0.25	5000	46.37
"	Tetrabutylammonium hydroxide	1: 0.50	5000	37.36
"	Tetrabutylammonium hydroxide	1: 1	5000	25.37
"	Coco oxyalkylate	1: 0.25	5000	50.22
"	Coco oxyalkylate	1: 0.5	5000	41.87
"	Coco oxyalkylate	1: 1	5000	45.56

[00177] Example 5. Measuring the stability of asphaltenes. Asphaltene stability was assessed using analytical centrifuge which spun samples fixed horizontally on a flat rotor while the transmittance of near-infrared (NIR) light shone through the entire sample length was measured. A multi-position rotor

allowed for the simultaneous analysis of up to 12 samples. In the test a 0.1 ml sample of crude was diluted 40:1 with heptane and the solution placed in a cell in the centrifuge. By monitoring changes in light transmission along an entire length of a sample during centrifugation, changes in the dispersion's solid concentration at various levels of the sample could be detected. As the dispersed solids scattered light, light transmission increased in areas losing solids and decreased (if not already opaque) in areas gaining solids. Centrifugal force on the sample could be controlled from 5 to 2300 x g and temperature could be controlled from 4 to 60°C. Sample size ranged from 0.1 to 2 mL depending on the centrifuge vials used. The centrifuge was started and the amount of asphaltene precipitation as a function of time was measured using a laser light source shining through the sample as it rotated. Asphaltene stability index was calculated by the instrument from the change in light transmittance through the sample as a function of time. This calculation parameter was termed the instability index; the instability index being a calculation of the change in integral transmission between time t and time 0, normalized by the maximum theoretical transmission, resulting in a calculated value from 0 to 1.0. A instability index of zero means the asphaltenes are very stable and did not precipitate. Higher instability index values indicate asphaltene instability and precipitation had occurred.

[00178] In all test runs below, the resin based ionic liquid was prepared by mixing the p-dodecylphenol/ formaldehyde acid catalyzed resin with the ionic liquid (cation:anion mentioned) to make a new ionic liquid product. This material was shaken for 5 minutes and then added to the crude. The amount of resin and original ionic liquid cation:anion) used in the test was listed below.

All preparations and test were done at room temperature. The results are shown in Table II.

Table II

Resin	Cation	Anion	Resin/IL Dose (ppm)	Crude Instability Index
Untreated Crude oil	None	None	0	0.375
p-dodecylphenol/formaldehyde acid catalyzed resin	None	None	40	0.156
"	Tetra n-butylammonium		40/10	0.133
"	Tri-n-butylmethylammonium	CH_3CO_3^-	40/10	0.078
"	Tetraethylammonium	HCO_3^-	40/10	0.090
"	$\text{Coco}(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{OH})\text{N}^+$	OH^-	40/10	0.208
"	$\text{Coco}(\text{CH}_3)_3\text{N}^+$	OH^-	40/10	0.175
"	$\text{Coco}(\text{CH}_3)_3\text{N}^+$	CH_3CO_3^-	40/100	0.340
"	$\text{Coco}(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{CH}_2$	$\text{CH}_3\text{OC}_2\text{O}_2^-$	40/10 40/100	0.140 0.099
"	$\text{Coco}_2(\text{CH}_3)_2\text{N}^+$	OH^-	40/30	0.077

[00179] Example 6. Acid reduction using ionic liquids. A specified amount of a quaternary ammonium hydroxide was added to the hydrocarbon sample. The sample was then shaken for 5 minutes. A sample of the treated oil was tested, using ASTM D664. The results are shown in Table III for acid content.

Table III

Hydrocarbon	Additive	Dosage ppm(v)	TAN (mg KOH / g)
B100 biodiesel	None	0	0.68
"	Tetraethylammonium hydroxide	700	0.26
"	"	1400	0.05
"	Benzyltrimethylammonium hydroxide	400	0.41
"	"	800	0.19
Crude Oil	None	0	3.59
"	Tetraethylammonium hydroxide	500	3.14
"	"	750	---
"	"	1000	2.74

Hydrocarbon	Additive	Dosage ppm(v)	TAN (mg KOH / g)
“	“	1500	2.45
“	“	2000	2.08
“	“	2500	1.64
“	“	3000	1.25
“	Tetrapropylammonium hydroxide	1000	2.90
“	“	1500	2.69
“	“	2000	2.35
“	“	2500	2.11
“	“	3000	1.82
Diesel Fuel	“	0	7.81
“	Benzyltrimethylammonium hydroxide	1000	6.92
“	Coco dimethyl ethylammonium methyl carbonate	1000	7.06
“	Dodecyl trimethylammonium hydroxide	1000	7.06
“	Tetra – n-butylammonium hydroxide	1000	7.07
“	Coco trimethylammonium methylcarbonate	1000	7.24
“	Tetraethylammonium bicarbonate	1000	7.26
“	(2-hydroxyethyl) coco dimethylammonium hydroxide	1000	7.26
“	Tri-n-butyl methylammonium methylcarbonate	1000	7.28

[00180] Example 7. Ionic Liquids as hydrogen sulfide scavengers.

Samples of sour gasoline were treated with the additive, shaken and then left standing at room temperature for 1 hour. The samples were then analyzed for H₂S content by pipetting liquid hydrocarbon into isopropyl alcohol containing a small amount of ammonium hydroxide. The solution was titrated potentiometrically with alcoholic silver nitrate using a glass reference and silver-silver sulfide indicating electrode system. With the mercaptan test, ethyl mercaptan (130 ppm) was added to a hydrocarbon sample, the hydrocarbon was treated with scavenger, shaken and left standing for 1 hour. Mercaptan content was then determined. The results are shown in Table V.

Table V

Sample	H ₂ S Conc. in Liquid (ppm)	EtSH Conc. In Liquid (ppm)
Untreated	58	130
Tetraethylammonium bicarbonate	37	118
Tetra-n-butylammonium hydroxide	21	0

[00181] Example 8. Ionic liquids in sulfur extraction. A 20 ml sample of gasoline from Philadelphia Energy Solutions refinery was shaken for 5 minutes with 20 ml of 35% aqueous tetraethylammonium hydroxide. The hydrocarbon and aqueous layers were allowed to separate and the two phases collected. The hydrocarbon phase was analyzed for total sulfur content by x-ray fluorescence and the aqueous phase was mixed with fresh 20 mls of gasoline and the procedure was repeated for 4 cycles. The amount of sulfur the ionic liquid could remove before it became saturated and could no longer extract sulfur compounds from the hydrocarbon was determined. With each cycle, the sulfur content of the separated gasoline increased as the ionic liquid solution's capacity to remove it decreased as set forth in Table VI.

Table VI

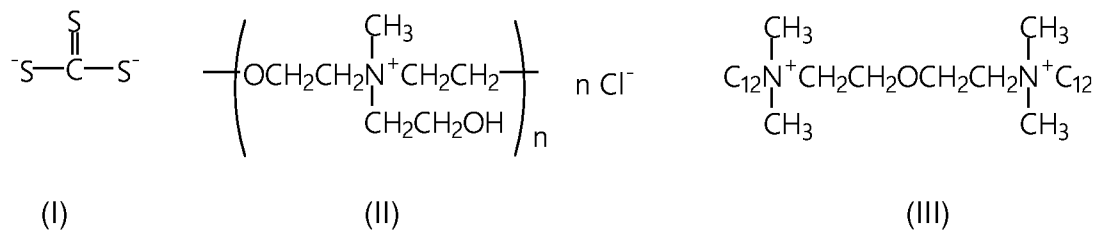
Contact Cycle	Total Gasoline Sulfur Content after Extraction (ppm)
Untreated	39.4
Cycle 1	13.7
Cycle 2	15.7
Cycle 3	17.8
Cycle 4	20.5

[00182] Example 9. Preparation of ionic liquids for use in wastewater treatment. Synthesis of ionic liquids was performed using an anion replacement technique. Quaternary ammonium halides (chlorides)

(represented by B and C, below) were mixed with sulfur based anions (represented by trithio carbonate) to make the ionic liquid and potassium chloride. These products were all aqueous based materials so the potassium chloride by-product was soluble and remained in the product tested.

[00183] A general procedure for preparing the ionic liquid may be represented by the following wherein about 20 g of a solution of 25% di sodium trithiocarbonate in water was mixed with elemental sulfur (2 grams) and heated to 60 °C with stirring until sulfur dissolved. 7.8 grams of a solution of 36% active oxy di-2,1-ethanediyl) bis(cocodimethylammonium) dichloride in water and methanol (1:1) was added dropwise and the mixture stirred as it cooled back to room temperature. The product was then tested as is without further modification.

Raw materials used in the synthesis were:



A test was conducted where the additive was added to the test material in a 4 oz bottle and the mixture shaken for five to ten minutes. The samples were allowed to settle and the samples were removed for metal analysis by GC-mass spec (zinc, copper) or an elemental analyzer (mercury). The results are set forth in Table VII below.

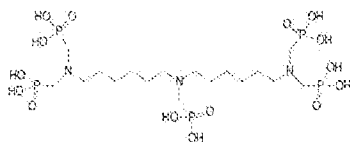
Table VII

Test Material	Sample*	Active Dose (ppm)	Copper (ppb)	Zinc (ppb)	Hg (ppb)
Wastewater	Untreated	50	402	12	---
"	B/trithiocarbonate IL	50	< 10*	< 10*	---
"	B/sulfurized trithiocarbonate IL	50	< 10*	<10*	---
"	Tetrabutylammonium thioglycolate IL	50	210*	12*	---
Oilfield condensate (hydrocarbon)	Untreated	0	---	---	669
	B/sulfurized (C)	33	---	---	140
	B/sulfurized thiocyanate	33	---	---	165
	B/sulfurized trithiocarbonate IL	34	---	---	258
	Tetraethylammonium sulfurized trithiocarbonate	33	---	---	395
	B/thiocyanate (-SCN)	56	---	---	469
	Tetraethylammonium/sulfurized mercaptoacetate IL	35	---	---	87

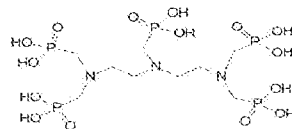
*Samples tested with 40 ppm or of a coagulant & 2 ppm of a flocculant were added to the water.

[00184] Example 10. Preparation of ionic liquids for scale control. A neutralization method was used to prepare ionic liquids for scale control. The general procedure may be represented by the following wherein about 5 grams (0.012 mole) of 35% tetraethylammonium hydroxide in water was added dropwise to 10 grams (0.006 mole) of (phosphonate of diethylenetriamine), represented by A below. The mixture was stirred for 30 minutes at room temperature and then tested without further modification.

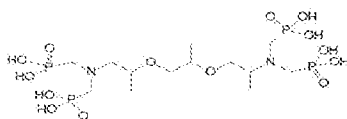
[00185] The scale inhibitors tried in the testing include:



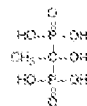
(A)



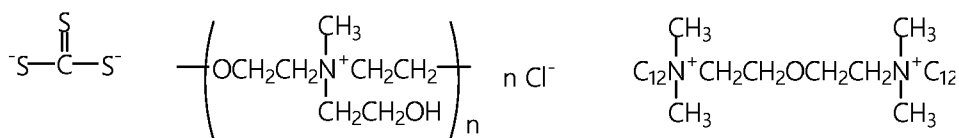
(B)



(C)



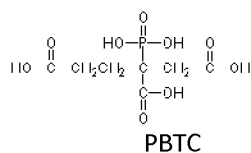
(D)



(E)

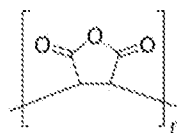
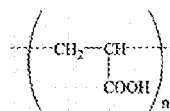
(F)

(G)



PBTC

(H)

(I) polyacrylate
copolymer salt

(J)

[00186] Cation and anion solutions of each brine were prepared. The pH of each anion solution was adjusted by purging carbon dioxide and nitrogen. Then 50 mL anion solutions were put into a series of 4 oz. bottles and the desired amount of scale inhibitor was dosed into the bottles. After shaking

thoroughly to mix anion solution and scale inhibitors, 50 mL cation solutions were added to each bottle, and these bottles were immediately inverted several times to assure thorough mixing of the components. Control and blank samples were also prepared. The control sample contained the mixture of the same volume of cation solution and deionized water to simulate the case without scale formation. The blank sample contained equal mixtures of anion and cation water to represent a brine with no protection against scale formation. All bottles were capped and placed in an oven with the designed heating temperature for a designed testing time. Visual observations of the resulting inhibited solutions were made initially, 2 hours, and 24 hours, and 72 hours after the addition of each scale inhibitor.

[00187] A Kinetic Turbidity Test was conducted with an Agilent Cary 100/300 series ultraviolet-visible (UV-Vis) spectrophotometer, which measured the absorbance of the sample solutions at a certain wavelength. Up to 12 samples were under temperature control, in a multi-sample holder with magnetic stirring in all cells. The samples could be tested simultaneously at temperatures ranging from 4°C to 95°C with designed cuvettes that were usually made of quartz. Each cuvette had a small hole on the bottom to hold a small magnetic stir bar. To conduct the test, a cuvette was placed in the first cell holder with 3 mL of deionized water to establish the baseline for turbidity. Anion brine was first added to the sample cuvettes. Various concentrations of inhibited anion brine were then added to each of the remaining cuvettes. Immediately before the start of the test, cation brine was then added to each of these cuvettes. The spectrophotometer reads results every 2 minutes, with a 5-second measurement time per cuvette over an approximate 2-hour

period. The kinetics application used the absorbance versus time data to determine the rate of reaction. This function recorded scale formation kinetics and differentiated scale inhibitor performance by observing how fast absorbance increased. The faster the absorbance observed, the faster the scale formation. The wavelength for analysis of turbidity was 500 nm for the kinetic function. The exemplary results are set forth in Table VII below.

Table VII

Scale inhibitor	Quat	Quat/ Inhibitor Molar Ratio	Compatibility Testing 2 Hr @ 70 °C			24 Hr @ 70 °C MEC (ppm)	KTT 2 hr MEC (ppm)
			@ 100 ppm	@1,000 ppm	@10,000 ppm		
A	None	---	Clear	Floc	Clear	3	3
A	TEAH	1.0	Floc	Floc	Floc	2-3	3
A	K	0.5	Clear	Floc	Clear	3-5	< 3
B	None	---	Clear	Clear	Clear	5	2
B	TEAH	1.0	Clear	Floc	Clear	5	
"	TEAH	2.0	Clear	Floc	Floc	3	3
"	TEAH	4.0	Clear	Floc	Floc	3	---
I	None	---	Clear	Clear	Floc	10	10
	TEAH	0.5	Clear	Slight cloudy	Floc	5	5
	TEAH	1.0	Clear	Clear	Floc	5	10
K	K	0.3	Clear	Clear	Clear	5	5
J	None	---	Clear	Floc	Less Floc	>5	3
	TEAH	4.0	Clear	Floc	Less Floc	5	5
	TBAH	4.0	Clear	Floc	Less Floc	5	---
H	None	---	Clear	Clear	Clear	> 5	
	TEAH	2.0	Clear	Clear	Clear	5	2
I	None	---	---	---	---	5	3
	TBPH	1.0	Clear	Floc	Clear	5	2

TEAH = tetraethylammonium. TBAH = tetrabutylphosphonium, K = methylated triethanolamine polymer

[00188] While exemplary embodiments of the disclosure have been shown and described, many variations, modifications and/or changes of the system, apparatus and methods of the present disclosure, such as in the components, details of construction and operation, arrangement of parts and/or methods of use, are possible, contemplated by the patent applicant(s), within the scope of the appended embodiments, and may be made and used by one of ordinary skill in the art without departing from the spirit or teachings of the disclosure and scope of appended embodiments. Thus, all matter herein set forth should be interpreted as illustrative, and the scope of the disclosure and the appended embodiments should not be limited to the embodiments described and shown herein.

CLAIMS

What is claimed is:

1. An ionic liquid of the formula:



wherein at least one A is or contains phosphorus or a phosphorus containing ring and the other A is or contains either phosphorus or nitrogen or a phosphorus or nitrogen containing ring; and wherein X is an anion selected from the group consisting of halides; hydroxyl; carbonates; alkyl carbonates; bicarbonates; carboxylates; hydroxycarboxylates; anionic dithiocarbonates; anionic trithiocarbonates; xanthates, thiocyanates; alkoxides; anionic urea; anionic alkyl substituted phosphines; anionic amino fatty acids; anionic alkoxyated fatty acids; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic phosphated maleic copolymers; anionic homo or copolymers of an oxirane or methyloxirane; anionic metal complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic oxirane or methyloxirane homo or copolymers; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic alkyl substituted phosphines; anionic copolymers of ethylene and vinyl acetate; and anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates, acrylamides, methylated acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers; and mixtures thereof; and further wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are independently selected

from the group consisting of hydrogen; benzyl; alkylbenzyl, or oxyalkyl; a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

2. An ionic liquid of formulas:



wherein A is or contains phosphorus or a phosphorus containing ring and X is an anion selected from the group consisting of hydroxyl; bicarbonates; alkoxides; anionic hydroxycarboxylates; silicon containing anions; anionic amino fatty acids; anionic alkoxylated fatty acids; anionic thiophosphonate esters; alkyl substituted phosphines; anionic urea; anionic thiourea; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers; anionic copolymers of ethylene and vinyl acetate; phosphated maleic copolymers; an anionic homo or copolymer of an oxirane or methyloxirane and mixtures thereof.

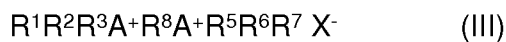
3. An ionic liquid of formulas:



wherein A is or contains nitrogen or a nitrogen heterocyclic ring and the anion X is selected from the group consisting of silicon containing anions; anionic thiophosphonate esters; anionic natural products; anionic phenol resins; alkoxides; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof or a mixture thereof; amino fatty acids; anionic alkoxyated fatty acids; alkyl substituted phosphines; anionic urea; anionic thiourea; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers containing acrylamide units; phosphated maleic copolymers; anionic copolymers of ethylene and vinyl acetate; oxirane or methyloxirane homo or copolymers; and mixture thereof; and R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from the group consisting of hydrogen; benzyl; alkylbenzyl, or oxyalkyl; a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion.

4. An ionic liquid of formulas:

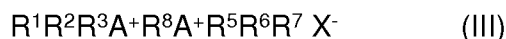




wherein A in formula (II) is nitrogen or a nitrogen containing ring and each A in formula (III) is nitrogen as defined herein and wherein X is an anion selected from the group consisting of anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof amino fatty acids; anionic oxirane or methyloxirane homo or copolymers; anionic alkoxyated fatty acids; anionic phosphonic acid; anionic diposphonic acid; anionic alkyl substituted phosphines; anionic urea; anionic thiourea; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic copolymers of ethylene and vinyl acetate; anionic homopolymers, copolymers and terpolymers containing acrylamide units; phosphated maleic copolymers and mixtures thereof; and further wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from the group consisting of hydrogen; benzyl; alkylbenzyl, or oxyalkyl; a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

5. A method of treating a hydrocarbon containing fluid to:
- (a) remove metals, amines and/or phosphorus compounds from the fluid;
 - (b) reduce the viscosity of the fluid;
 - (c) remove organic acids or inorganic salts from the fluid;
 - (d) reduce concentration of naphthenic acid content in the fluid;
 - (e) inhibit or prevent fouling of contaminants onto a conduit or vessel in contact with the fluid or in a reservoir or refinery in which the fluid is produced or processed;
 - (f) inhibit the formation or deposition of contaminants within a refinery, in a reservoir, during transport of the fluid or during storage of the fluid; and/or
 - (g) clarify wastewater originating from the fluid.

comprising contacting the hydrocarbon containing fluid with any of the ionic liquids of claims 1 to 5 or an ionic liquid of the formulas:



wherein:

A in formula (II) is a nitrogen or phosphorus or a heterocyclic ring thereof and wherein each A in formula (III) is independently selected from nitrogen or phosphorus or a heterocyclic ring thereof; and further wherein

X is an anion selected from the group consisting of halides; hydroxyl; carbonates; alkyl carbonates; bicarbonates; carboxylates; hydroxycarboxylates; dithiocarbonates; trithiocarbonates; xanthates, thiocyanates; alkoxides; anionic urea; anionic alkyl substituted phosphines;

anionic amino fatty acids; anionic alkoxyated fatty acids; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic phosphated maleic copolymers; anionic homo or copolymers of an oxirane or methyloxirane; anionic metal complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic alkyl substituted phosphines; and anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers; and mixtures thereof; and further wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from the group consisting of hydrogen; benzyl; alkylbenzyl, or oxyalkyl; an oxirane or methyloxirane homo or copolymer; a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R^8 is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

6. The method of claim 5, wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently -H or a C_{1-20} alkyl.

7. The method of claim 5 or 6, wherein the anion is a halide selected from the group consisting of -Cl, -Br, -F or -I.

8. A method of treating a hydrocarbon containing fluid comprising contacting the hydrocarbon containing fluid with any of the ionic liquids of claims 1 to 5 or an ionic liquid of the formula:



wherein A is or contains nitrogen, a nitrogen containing heterocyclic ring, phosphorus or a phosphorus containing heterocyclic ring; and wherein:

when A is or contains phosphorous or a phosphorus containing ring, X⁻ is an anion selected from the group consisting of halides; hydroxyl; carbonates; alkyl carbonates; bicarbonates; anionic dithiocarbonates; anionic trithiocarbonates; xanthates, thiocyanates; alkoxides; anionic carboxylates; anionic hydroxycarboxylates; amino fatty acids; anionic alkoxylated fatty acids; anionic metallic complexes, sulfur or silicon containing anions; anionic phosphate esters, anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; alkyl substituted phosphines; anionic urea; anionic thiourea; anionic natural products; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic phenols; anionic phenol resins; alkoxides; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated

monomers; phosphated maleic copolymers; an anionic homo or copolymer of an oxirane or methyloxirane and mixtures thereof or a zwitterion; and

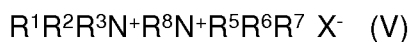
when A is or contains nitrogen or a nitrogen-containing heterocyclic ring; X is an anion selected from the group consisting of anionic metallic complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles ; anionic natural products; anionic phenols; anionic phenol resins; anionic alkoxides; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof or a mixture thereof; amino fatty acids; anionic alkoxylated fatty acids; alkyl substituted phosphines; anionic urea; anionic thiourea; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates and acrylamides, optionally copolymerized with one or more ethylenically unsaturated monomers; phosphated maleic copolymers and mixture thereof or a zwitterion.

9. A method of treating a hydrocarbon containing fluid to:

(a) inhibit or prevent the formation or precipitation of asphaltenes in the fluid; or

(b) remove or reduce sulfur containing compounds in the fluid,

the method comprising contacting the fluid with an ionic liquid of the formula:



X is an anion selected from the group consisting of halides; hydroxyl; carbonates; alkyl carbonates; bicarbonates; carboxylates; hydroxycarboxylates; sulfonates; sulfates; bisulfites; thiocyanates; dithiocarbonates; dithiocarbonates; trithiocarbonates; carbamates; dithiocarbamates; trithiocarbamates; xanthates; sulfides; polysulfides; alkoxides; anionic ureas; anionic alkyl substituted phosphines; anionic amino fatty acids; anionic alkoxyfatty acids; anionic acrylamido-methyl propane sulfonate/acrylic acid copolymers; anionic phosphated maleic copolymers; anionic metal complexes; sulfur or silicon containing anions; anionic phosphate esters; anionic thiophosphate esters; anionic phosphonate esters; anionic thiophosphonate esters; anionic thiols; anionic thiazoles, triazoles and thiadiazoles; anionic natural products; anionic phenols; anionic phenol resins; anionic copolymers of alpha olefins and maleic anhydride, esters, amides, imides or derivatives thereof; anionic alkyl substituted phosphines; and anionic homopolymers, copolymers and terpolymers of one or more acrylates, methacrylates, acrylamides and acids, optionally copolymerized with one or more ethylenically unsaturated monomers; anionic homo and copolymers of oxirane and/or methyloxirane; anionic copolymers of olefins and vinyl acetate; and mixtures thereof; and further wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are independently selected from the group consisting of hydrogen; benzyl; alkylbenzyl, or oxyalkyl; a straight or branched alkyl group, an alkylbenzyl group, an arylalkyl group, a straight or branched chain alkenyl group, a hydroxyalkyl group or a hydroxyalkylbenzyl group; and a polyoxyalkylene group; and R⁸ is a straight or branched alkylene group, an alkylene oxyalkylene, or an alkylene polyoxyalkylene or a zwitterion; and

further wherein R groups may be joined to form a heterocyclic nitrogen, sulfur or phosphorus containing ring.

10. The method of claim 9, wherein the ionic liquid is an asphaltene inhibitor.

11. The method of claim 10, wherein X is an anionic phenol aldehyde resin.

12. The method of claim 9, wherein the ionic liquid removes or reduces sulfur containing compounds.

13. The method of claim 12, wherein X of the ionic liquid is selected from the group consisting of anionic triazines, anionic amine aldehyde condensates, anionic aldehydes, anionic diaminomethanes and mixtures thereof.

14. The method of any of claims 5 to 13, wherein the ionic liquid is a component of a treatment composition and wherein the treatment composition further contains a treatment agent.

15. The method of claim 14, wherein the anion of the treatment agent and the anion of the ionic liquid are the same.

16. The method of any of claims 5 to 15, wherein the hydrocarbon containing fluid is gas cuts, crude oil, coker distillate, alkylate, reformat, cycle oil, bitumen, diesel fuel, biofuel, a residual oil or a hydrotreated hydrocarbon.

17. The method of any of claims 5 to 16, wherein the hydrocarbon containing fluid is:

- (A) a fluid produced from a subterranean formation penetrated by a reservoir;
- (B) a fluid introduced into a subterranean formation penetrated by a reservoir;
- (C) a fluid introduced into a conduit or vessel (i) in a refinery or (ii) in an underground reservoir or extending from or to an underground reservoir;
- (D) a fluid processed in a refinery;
- (E) wastewater; or
- (F) a petroleum hydrocarbon fluid.

18. The method of any of claims 5 to 17, wherein contacting of the hydrocarbon containing fluid with the ionic liquid or ionic liquid containing composition occurs during production, storage, transportation, or the refining of the hydrocarbon containing fluid.

19. The method of any of claims 5 to 8 and 14 to 18, wherein the ionic liquid inhibits or prevents the formation or deposition of scales.

20. The method of claim 19, wherein the ionic liquid is selected from the group consisting of anionic amino phosphonates, anionic diphosphonic acids and anionic homopolymers or copolymers of acrylic acid and mixtures thereof.

21. The method of claim 19 or 20, wherein the ionic liquid is present in a treatment composition containing a scale inhibitor selected from the group consisting of amino phosphonates, diphosphonic acids and homopolymers or copolymers of acrylic acid and mixtures thereof.

22. The method of any of claims 5 to 8 and 14 to 18, wherein the ionic liquid is capable of removing metal from wastewater.

23. The method of claim 22, wherein the ionic liquid is selected from the group consisting of anionic trithiocarbonates, anionic dithiocarbamates, anionic xanthates, anionic thiocyanates and anionic thioruea and mixtures thereof.

24. The method of claim 22 or 23, wherein the ionic liquid is present in a treatment composition and wherein the treatment agent is selected from the group consisting of trithiocarbonates, dithiocarbamates, xanthates, thiocyanates and thioruea and mixtures thereof.

25. The method of any of claims 5 to 8 and 14 to 18, wherein the ionic liquid is a water clarifier.

26. The method of claim 25, wherein the ionic liquid is an anionic polyacrylate.

27. The method of claim 24 or 25, wherein the ionic liquid is present in a treatment composition containing an anionic polyacrylamide.

28. The method of any of claims 5 to 8 and 14 to 18, wherein the ionic liquid inhibits or prevents fouling of contaminants.

29. The method of any of claims 5 to 8 and 14 to 18, wherein the ionic liquid is capable of removing contaminants or acids from wastewater.

30. The method of claim 29, wherein the ionic liquid is at least one member selected from the group consisting of:

(A) quat hydroxides of the formula $R_4^+ OH^-$ where R_4 is a C_1 - C_{18} alkyl group;

(B) sodium borohydride; and

(C) a caustic selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof.