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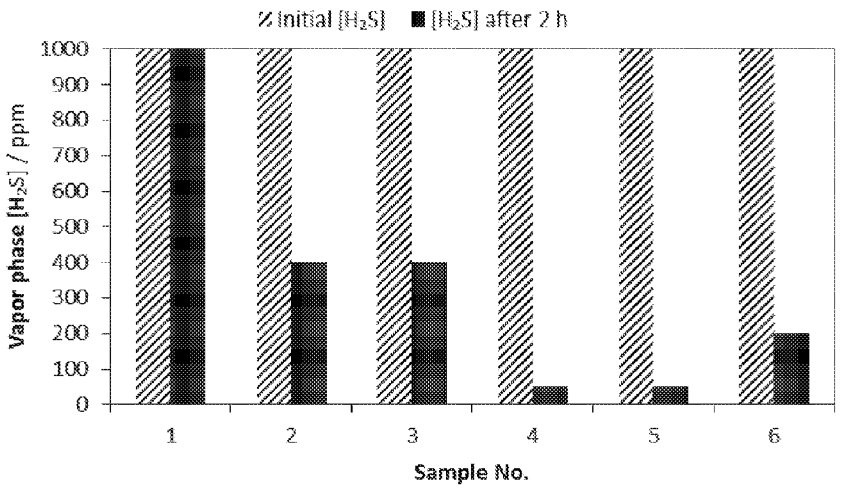
# (54) Title: HEAVY AMINES AS HYDROGEN SULFIDE AND MERCAPTAN SCAVENGERS

Figure 1



**(57) Abstract:** The present invention generally relates to compositions and methods for scavenging hydrogen sulfide and/or mercaptans from fluids. More particularly, the invention relates to the use of compositions comprising a surfactant and the reaction product between a polyamine and a formaldehyde as a hydrogen sulfide or a mercaptan scavenger for hydrocarbon-containing fluids, particularly for natural gas, crude oil, field oil, fuel oil, naphtha, gasoline, kerosene, diesel, slurry oil, gas oil, resid, refinery gas, coal gas, tar, asphalt, coke gas, ammonia synthesis gas, gas from an industrial gas stream, or a sulfurization plant.

*[Continued on next page]*

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**Declarations under Rule 4.17:**

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— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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# HEAVY AMINES AS HYDROGEN SULFIDE AND MERCAPTAN SCAVENGERS

## FIELD OF THE INVENTION

**[0001]** The present invention generally relates to compositions and methods for scavenging hydrogen sulfide and/or mercaptans from fluids. More particularly, the invention relates to the use of compositions comprising a surfactant and the reaction product between a polyamine and a formaldehyde as a hydrogen sulfide or a mercaptan scavenger for hydrocarbon-containing fluids, particularly for natural gas, crude oil, field oil, fuel oil, naphtha, gasoline, kerosene, diesel, slurry oil, gas oil, resid, refinery gas, coal gas, tar, asphalt, coke gas, ammonia synthesis gas, gas from an industrial gas stream, or a sulfurization plant.

## BACKGROUND OF THE INVENTION

**[0002]** Hydrogen sulfide ($H_2S$) is a very toxic, corrosive, flammable, explosive gas that causes problems in both upstream and downstream operations within the oil and gas industry. Exposure to this gas, even at low concentrations, can cause serious human injury or death. Hydrogen sulfide in natural gas and crude oil reserves is often accompanied by small amounts of mercaptans (RSH), sulfides ($R_2S$), polysulfides, and carbonyl sulfide (COS). Considerable expense and effort are expended annually to reduce the amount of $H_2S$ within gas and oil streams to make them suitable for commercial use.

**[0003]** Natural gas and crude oil streams containing substantial amounts of $H_2S$ are considered “sour.” In addition to natural gas and petroleum, there are also aqueous fluids that must be treated to reduce or remove $H_2S$, such as waste water streams. Treatments to reduce or remove $H_2S$ from hydrocarbon or aqueous streams are referred to as “sweetening” treatments because the odor of the processed products is improved by the absence of hydrogen sulfide. A chemical compound that is used to remove or reduce $H_2S$ levels sometimes is called a “scavenger” or “scavenging agent.” Scavengers that react irreversibly with hydrogen sulfide or other sulfur species and convert them to a more inert form are considered nonregenerative.

**[0004]** In large production facilities, the most economical solution to remove $H_2S$ from a sour gas stream is to install a regenerative system. These systems typically employ a compound used in an absorption tower to contact the produced fluid and selectively absorb the $H_2S$ and other toxic compounds such as mercaptans. These systems typically employ alkanolamine as absorption compounds. Typical alkanolamine include N-methyldiethanolamine (MDEA), diethanolamine (DEA), monoethanolamine (MEA) and diglycolamine (DGA). This process is known as gas sweetening. The absorption compound(s) and $H_2S$ are then regenerated by various means including heat, pressure reduction, or a combination thereof. The absorption compound(s) is/are reused in the system, and the separated $H_2S$ is treated by a modified Claus process to form elemental sulfur.

**[0005]** For hydrocarbon streams with small concentrations of $H_2S$, the use of scavengers in batch or continuous injection treatments can provide a cost-effective alternative to conventional gas/liquid sweetening processes. Known hydrogen sulfide scavengers includes solid scavengers (e.g. zinc-based or iron-based materials), oxidizing chemicals (e.g. chlorites, nitrites, bromates, iodates, and peroxides), aldehydes (e.g. formaldehyde, glutaraldehyde, acrolein, and glyoxal), reaction products of aldehydes and amines (e.g. triazines), metal carboxylates and other chelates, and other amine based products (e.g. amidines, maleimides, and amine oxides).

**[0006]** Some of these known hydrogen sulfide scavengers may be corrosive to some metals such as steel, iron, and aluminum which can be detrimental to the infrastructure used within the upstream and downstream operations within the oil and gas industry.

**[0007]** Thus, there is a need to develop alternative chemistries that overcome these deficiencies.

## SUMMARY OF THE INVENTION

**[0008]** One aspect of the invention is directed to a method of reducing the amount of hydrogen sulfide or mercaptans in a hydrocarbon-containing fluid. The method comprises contacting an effective amount of a scavenger composition with a hydrocarbon-containing fluid. The scavenger composition comprises a surfactant and a reaction product of a polyamine and formaldehyde.

**[0009]** Other objects and features will be in part apparent and in part pointed out hereinafter.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]** Figure 1 is a graph of $H_2S$ reduction of sour fuel oil treated with various polyalkylamine/formaldehyde reaction products at a dose ratio of polyalkylamine/formaldehyde reaction products to initial $H_2S$ concentration of 0.4.

**[0011]** Figure 2 is a graph of $H_2S$ reduction of sour kerosene treated with various polyalkylamine/formaldehyde reaction products at a dose ratio of polyalkylamine/formaldehyde reaction products to initial $H_2S$ concentration of 0.8.

**[0012]** Figure 3 is a graph of $H_2S$ reduction of sour kerosene vs. dosage of diethylenetriamine/formaldehyde.

**[0013]** Corresponding reference characters indicate corresponding parts throughout the drawings.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0014]** Due to the safety considerations of having high concentrations of hydrogen sulfide and mercaptan compounds in hydrocarbon fluids, new hydrogen sulfide and mercaptan scavengers are needed that have improved health, environmental, and safety profiles. The scavenger compositions of a surfactant and a reaction product of a polyamine and formaldehyde described herein provide rapid, efficient, and effective reduction of hydrogen sulfide and mercaptan while being less corrosive to metal in the processing and transportation equipment than traditional scavengers.

**[0015]** The present invention is directed towards a method of reducing the amount of hydrogen sulfide or mercaptans in a hydrocarbon-containing fluid. The method comprises contacting an effective amount of a scavenger composition with a hydrocarbon-containing fluid. The scavenger composition comprising a surfactant and a reaction product of a polyamine and formaldehyde.

**[0016]** The hydrocarbon-containing fluid can comprise crude oil, field oil, asphalt, naphtha, gasoline, kerosene, diesel, natural gas, refinery gas, coal gas, coke gas, ammonia synthesis gas, an industrial gas stream, or gas from a sulfurization plant.

**[0017]** Preferably, the hydrocarbon-containing fluid can comprise crude oil.

**[0018]** The polyamine can comprise ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, tetrabutylenepentamine, hexaethyleneheptamine, hexapentyleneheptamine, heptaethyleneoctamine, octaethylenenonamine, nonaethylenedecamine, decaethyleneundecamine, decahexyleneundecamine, undecaethylenedodecamine, dodecaethylenetridecamine, tridecaethylenetetradecamine, N-tallow propylenediamine, or a combination thereof. The polyamine can comprise diethylenetriamine, tetraethylenepentamine, or a combination thereof.

**[0019]** The reaction product can comprise a molar ratio of formaldehyde to polyamine of from about 0.1:1 to about 25:1, from about 0.1:1 to about 20:1, from about 0.1:1 to about 15:1, from about 0.1:1 to about 10:1, from about 0.1:1 to about 5:1, from about 0.5:1 to about 25:1, from about 0.5:1 to about 20:1, from about 0.5:1 to about 15:1, from about 0.5:1 to about 10:1, from about 0.5:1 to about 5:1, from about 1:1 to about 25:1, from about 1:1 to about 20:1, from about 1:1 to about 15:1, from about 1:1 to about 10:1, from about 1:1 to about 5:1, or from about 1:1 to about 2:1.

**[0020]** Preferably, the reaction product can comprise a molar ratio of formaldehyde to polyamine of from about 1:1 to about 5:1 or from about 1:1 to about 2:1.

**[0021]** The surfactant can comprise a quaternary ammonium compound, a trialkylamine oxide, alkoxylated alkylalcohol, or a combination thereof. Preferably, the surfactant can comprise a tetraalkyl ammonium chloride, a tetraalkyl ammonium sulfate, a ($C_8$-$C_{20}$alkyl)di($C_1$-$C_4$alkyl) amine oxide, ethoxylated $C_4$-$C_{14}$ alcohol, or a combination thereof.

**[0022]** More preferably, the surfactant can comprise tetralkyl ammonium chloride.

**[0023]** The surfactant can be added to the scavenger composition at a concentration of from about 0.5 to about 15 wt.%, from about 0.5 to about 12 wt.%, from about 0.5 to about 10 wt.%, from about 0.5 to about 9 wt.%, from about 0.5 to about 8 wt.%, from about 0.5 to about 7 wt.%, from about 0.5 to about 6 wt.%, from about 0.5 to about 5 wt.%, from about 1 to about 15 wt.%, from about 1 to about 12 wt.%, from about 1 to about 10 wt.%, from about 1 to about 9 wt.%, from about 1 to about 8 wt.%, from about 1 to about 7 wt.%, from about 1 to about 6 wt.%, from about 1 to about 5 wt.%, based on the total weight of the scavenger composition.

**[0024]** Preferably, the surfactant can be added to the scavenger composition at a concentration from about 1 to about 5 wt.%, based on the total weight of the scavenger composition and more preferably, the surfactant can be added to the scavenger composition at a concentration from about 4 to about 6 wt.%, based on the total weight of the scavenger composition.

**[0025]** The scavenger composition can be contacted with the hydrocarbon-containing fluid at a concentration from about 0.2 to about 5 ppm, from about 0.2 to about 4 ppm, from about 0.2 to about 3 ppm, from about 0.2 to about 2 ppm, from about 0.4 to about 5 ppm, from about 0.4 to about 4 ppm, from about 0.4 to about 3 ppm, or from about 0.4 to about 2 ppm, per 1 ppm of hydrogen sulfide or mercaptan detected in the vapor space of the hydrocarbon-containing fluid.

**[0026]** Preferably, the scavenger composition can be contacted with the hydrocarbon-containing fluid at a concentration from 0.4 to 0.8 ppm per 1 ppm of hydrogen sulfide or mercaptan detected in the vapor space of the hydrocarbon-containing fluid.

**[0027]** The scavenger composition can be contacted with the hydrocarbon-containing fluid at a temperature from about 20 °C to about 290 °C, from about 20 °C to about 280 °C, from about 20 °C to about 270 °C, from about 20 °C to about 260 °C, from about 20 °C to about 250 °C, from about 20 °C to about 240 °C, from about 20 °C to about 230 °C, from about 20 °C to about 220 °C, from about 20 °C to about 210 °C, from about 20 °C to about 200 °C, from about 20 °C to about 190 °C, from about 20 °C to about 180 °C, from about 20 °C to about 170 °C, from about 20 °C to about 160 °C, from about 20 °C to about 150 °C, from about 20 °C to about 140 °C, from about 20 °C to about 130 °C, from about 20 °C to about 120 °C, from about 20 °C to about 110 °C, from about 20 °C to about 100 °C.

**[0028]** Preferably, the scavenger composition can be contacted with the hydrocarbon-containing fluid at a temperature from about 20 °C to about 100 °C.

**[0029]** The rate of reaction between the hydrogen sulfide or mercaptan and the reaction product of a polyamine and formaldehyde can be increased using the scavenger composition as compared to the rate of reaction using the reaction product of a polyamine and formaldehyde in the absence of the surfactant.

**[0030]** The increased rate of reaction can be demonstrated by a reduction in the hydrogen sulfide or mercaptan concentration of 2, 3, 4, 5, 6, 7, 8, or more times during a residence time of 2 hours at 100°C.

**[0031]** The scavenger composition can be injected into, or otherwise brought into contact with, the hydrocarbon-containing fluid in any convenient manner. For example, the scavenger composition may be injected into the hydrocarbon-containing fluid upstream of a refining unit as the fluid passes through a turbulent section of piping. Also, the scavenger composition can be admixed with a hydrocarbon-containing fluid in a holding vessel that is agitated. Further, the scavenger composition can be admixed with the hydrocarbon-containing fluid immediately upstream of a refining unit by injecting it into a turbulent flow. Still further, the scavenger composition can be atomized and added to a vaporous hydrocarbon stream using, for example, an injection quill.

**[0032]** The methods can be performed wherein the scavenger composition is contacted with the hydrocarbon-containing fluid by injecting the composition into a run-down line for the hydrocarbon-containing fluid. The scavenger composition can also be injected into hydrocarbon-containing fluid using a bubble tower contactor. The scavenger composition can be injected as part of a continuous or batch process.

**[0033]** The methods can also include contacting the scavenger composition with the hydrocarbon-containing fluid by injecting the composition into a storage tank with mixing.

**[0034]** The scavenger composition may be formulated with a solvent, other suitable materials, or additives, such as dispersants and corrosion inhibitors. For liquid systems, suitable solvents for dissolving the compounds include polar and nonpolar solvents. Preferred solvents include methanol, heavy aromatic naphtha, light aromatic naphtha, 2-ethylhexanol, or a combination thereof.

**[0035]** The scavenger composition can be used with or without a solvent. When a solvent is used, the composition can be present at a concentration of from about 5 wt.% to about 95 wt.%, from about 5 wt.% to about 90 wt.%, from about 5 wt.% to about 85 wt.%, from about 10 wt.% to about 95 wt.%, from about 10 wt.% to about 90 wt.%, from about 10 wt.% to about 85 wt.%, from about 15 wt.% to about 95 wt.%, from about 15 wt.% to about 90 wt.%, from about 15 wt.% to about 85 wt.%, from about 20 wt.% to about 95 wt.%, from about 20 wt.% to about 90 wt.%, from about 20 wt.% to about 85 wt.%, from about 25 wt.% to about 95 wt.%, from about 25 wt.% to about 90 wt.%, from about 25 wt.% to about 85 wt.%, from about 30 wt.% to about 95 wt.%, from about 30 wt.% to about 90 wt.%, from about 30 wt.% to about 85 wt.%, from about 35 wt.% to about 95 wt.%, from about 35 wt.% to about 90 wt.%, or from about 35 wt.% to about 85 wt.%.

**[0036]** The scavenger composition can also be used in applications outside of a refining process. For example, when the application to be treated is an oil well, the scavenger composition can be introduced downhole or into the above ground equipment. The scavenger composition can also be introduced into pipelines, storage vessels, and mobile vessels such as trucks, rail cars, and ship cargo holds. The scavenger compositions can be actively or passively mixed with the hydrocarbon-containing fluid being treated.

**[0037]** Another aspect of the present invention is a method of reducing the amount of hydrogen sulfide or a mercaptan in an aqueous fluid having a high concentration of hydrogen sulfide or mercaptans. The method comprises contacting a scavenger composition with the aqueous fluid. The aqueous fluid can include an aqueous stream of a water injection system, waste water associated with a hydrocarbon treatment system, a waste water stream in transit to or from a wastewater treatment facility, or waste water from a tanning facility.

**[0038]** Generally, the reaction product of the polyamine and the formaldehyde are prepared by adding a polyamine to a round bottom flask and adding water slowly for 30 minutes; since the reaction is exothermic, the reaction temperature increases to about 55-60°C. After the reaction mixture cools to 50 °C, formalin (in about a 1.5:1 to 3:1 formalin:amine molar ratio) is added dropwise into the reaction mixture. The rate of formalin addition is adjusted to keep the reaction temperature between 50 °C and 66 °C. Once the addition was complete, the reaction mixture is stirred for 1 hour at 60-90 °C.

**[0039]** The scavenger composition can comprise an effective amount of the anticorrosion composition described herein and a component selected from the group consisting of an organic solvent, a corrosion inhibitor, an asphaltene inhibitor, a paraffin inhibitor, a scale inhibitor, an emulsifier, a water clarifier, a dispersant, an emulsion breaker, a gas hydrate inhibitor, a biocide, a pH modifier, a surfactant, and a combination thereof.

**[0040]** The scavenger composition can comprise from about 20 to about 90 wt.% of the scavenger composition and from about 10 to about 80 wt.% of the component, preferably from about 50 to about 90 wt.% of the scavenger composition and from about 10 to about 50 wt.% of the component, and more preferably from about 65 to about 85 wt.% of the scavenger composition and from about 15 to about 35 wt.% of the component.

**[0041]** The component of the composition can comprise an organic solvent. The composition can comprise from about 1 to 80 wt.%, from about 5 to 50 wt.%, or from about 10 to 35 wt.% of the one or more organic solvents, based on total weight of the composition. The organic solvent can comprise an alcohol, a hydrocarbon, a ketone, an ether, an alkylene glycol, a glycol ether, an amide, a nitrile, a sulfoxide, an ester, or a combination thereof. Examples of suitable organic solvents include, but are not limited to, methanol, ethanol, propanol, isopropanol, butanol, 2-ethylhexanol, hexanol, octanol, decanol, 2-butoxyethanol, methylene glycol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, diethyleneglycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dibutyl ether, pentane, hexane, cyclohexane, methylcyclohexane, heptane, decane, dodecane, diesel, toluene, xylene, heavy aromatic naphtha, cyclohexanone, diisobutylketone, diethyl ether, propylene carbonate, N-methylpyrrolidinone, N,N-dimethylformamide, or a combination thereof.

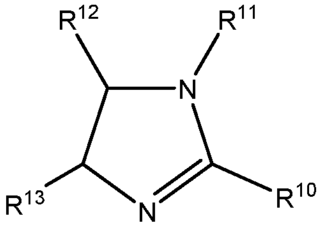
**[0042]** The component of the composition can comprise an additional corrosion inhibitor. The composition can comprise from about 0.1 to 20 wt. %, 0.1 to 10 wt.%, or 0.1 to 5 wt. % of the corrosion inhibitors, based on total weight of the composition. A composition of the invention can comprise from 0.1 to 10 percent by weight of the corrosion inhibitors, based on total weight of the composition. The composition can comprise 1.0 wt %, 1.5 wt %, 2.0 wt %, 2.5 wt %, 3.0 wt %, 3.5 wt %, 4.0 wt %, 4.5 wt %, 5.0 wt %, 5.5 wt %, 6.0 wt %, 6.5 wt %, 7.0 wt %, 7.5 wt %, 8.0 wt %, 8.5 wt %, 9.0 wt %, 9.5 wt %, 10.0 wt %, 10.5 wt %, 11.0 wt %, 11.5 wt %, 12.0 wt %, 12.5 wt %, 13.0

wt %, 13.5 wt %, 14.0 wt %, 14.5 wt %, or 15.0 wt % by weight of the corrosion inhibitors, based on total weight of the composition. Each system can have its own requirements, and the weight percent of one or more additional corrosion inhibitors in the composition can vary with the system in which it is used.

**[0043]** The corrosion inhibitor can comprise an imidazoline compound, a quaternary ammonium compound, a pyridinium compound, or a combination thereof.

**[0044]** The corrosion inhibitor component can comprise an imidazoline. The imidazoline can be, for example, imidazoline derived from a diamine, such as ethylene diamine (EDA), diethylene triamine (DETA), triethylene tetraamine (TETA) etc. and a long chain fatty acid such as tall oil fatty acid (TOFA). The imidazoline can be an imidazoline of Formula (I) or an imidazoline derivative. Representative imidazoline derivatives include an imidazolinium compound of Formula (II) or a bis-quaternized compound of Formula (III).

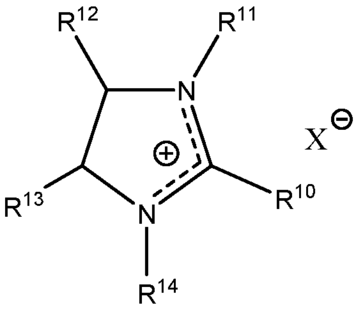
**[0045]** The corrosion inhibitor component can include an imidazoline of Formula (I):



(I)

wherein $R^{10}$ is a $C_1$-$C_{20}$ alkyl or a $C_1$-$C_{20}$ alkoxyalkyl group; $R^{11}$ is hydrogen, $C_1$-$C_6$ alkyl, $C_1$-$C_6$ hydroxyalkyl, or $C_1$-$C_6$ arylalkyl; and $R^{12}$ and $R^{13}$ are independently hydrogen or a $C_1$-$C_6$ alkyl group. Preferably, the imidazoline includes an $R^{10}$ which is the alkyl mixture typical in tall oil fatty acid (TOFA), and $R^{11}$, $R^{12}$ and $R^{13}$ are each hydrogen.

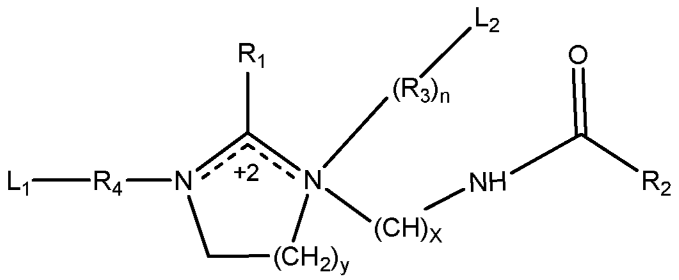
**[0046]** The corrosion inhibitor component can include an imidazolinium compound of Formula (II):



(II)

wherein $R^{10}$ is a $C_1$-$C_{20}$ alkyl or a $C_1$-$C_{20}$ alkoxyalkyl group; $R^{11}$ and $R^{14}$ are independently hydrogen, $C_1$-$C_6$ alkyl, $C_1$-$C_6$ hydroxyalkyl, or $C_1$-$C_6$ arylalkyl; $R^{12}$ and $R^{13}$ are independently hydrogen or a $C_1$-$C_6$ alkyl group; and $X^-$ is a halide (such as chloride, bromide, or iodide), carbonate, sulfonate, phosphate, or the anion of an organic carboxylic acid (such as acetate). Preferably, the imidazolinium compound includes 1-benzyl-1-(2-hydroxyethyl)-2-tall-oil-2-imidazolinium chloride.

**[0047]** The corrosion inhibitor can comprise a bis-quaternized compound having the formula (III):



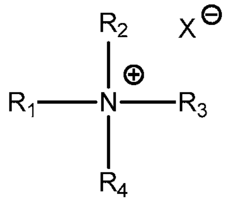
(III)

wherein $R_1$ and $R_2$ are each independently unsubstituted branched, chain or ring alkyl or alkenyl having from 1 to about 29 carbon atoms; partially or fully oxygenized, sulfurized, and/or phosphorylized branched, chain, or ring alkyl or alkenyl having from 1 to about 29 carbon atoms; or a combination thereof; $R_3$ and $R_4$ are each independently unsubstituted branched, chain or ring alkylene or alkenylene having from 1 to about 29 carbon atoms; partially or fully oxygenized, sulfurized, and/or phosphorylized branched, chain, or ring alkylene or alkenylene having from 1 to about 29 carbon atoms; or a combination thereof; $L_1$ and $L_2$ are each independently absent, H, -COOH, $-SO_3H$, $-PO_3H_2$, $-COOR_5$, $-CONH_2$, $-CONHR_5$, or $--CON(R_5)_2$; $R_5$ is each independently a branched or unbranched alkyl, aryl, alkylaryl, alkylheteroaryl, cycloalkyl, or heteroaryl group having from 1 to about 10 carbon atoms; n is 0 or 1, and when n is 0, $L_2$ is absent or H; x is from 1 to about 10; and y is from 1 to about 5. Preferably, $R_1$ and $R_2$ are each independently $C_6$-$C_{22}$ alkyl, $C_8$-$C_{20}$ alkyl, $C_{12}$-$C_{18}$ alkyl, $C_{16}$-$C_{18}$ alkyl, or a combination thereof; $R_3$ and $R_4$ are $C_1$-$C_{10}$ alkylene, $C_2$-$C_8$ alkylene, $C_2$-$C_6$ alkylene, or $C_2$-$C_3$ alkylene; n is 0 or 1; x is 2; y is 1; $R_3$ and $R_4$ are $-C_2H_2-$; $L_1$ is –COOH, $-SO_3H$, or $-PO_3H_2$; and $L_2$ is absent, H, –COOH, $-SO_3H$, or $-PO_3H_2$. For example, $R_1$ and $R_2$ can be derived from a mixture of tall oil fatty acids and are predominantly a mixture of $C_{17}H_{33}$ and $C_{17}H_{31}$ or can be $C_{16}$-$C_{18}$ alkyl; $R_3$ and $R_4$ can be $C_2$-$C_3$ alkylene such as $-C_2H_2-$; n is 1 and $L_2$ is –COOH or n is 0 and $L_2$ is absent or H; x is 2; y is 1; $R_3$ and $R_4$ are $-C_2H_2-$; and $L_1$ is –COOH.

**[0048]** It should be appreciated that the number of carbon atoms specified for each group of formula (III) refers to the main chain of carbon atoms and does not include carbon atoms that may be contributed by substituents.

**[0049]** The corrosion inhibitor can comprise a bis-quaternized imidazoline compound having the formula (III) wherein $R_1$ and $R_2$ are each independently $C_6$-$C_{22}$ alkyl, $C_8$-$C_{20}$ alkyl, $C_{12}$-$C_{18}$ alkyl, or $C_{16}$-$C_{18}$ alkyl or a combination thereof; $R_4$ is $C_1$-$C_{10}$ alkylene, $C_2$-$C_8$ alkylene, $C_2$-$C_6$ alkylene, or $C_2$-$C_3$ alkylene; x is 2; y is 1; n is 0; $L_1$ is–COOH, $-SO_3H$, or $-PO_3H_2$; and $L_2$ is absent or H. Preferably, a bis-quaternized compound has the formula (III) wherein $R_1$ and $R_2$ are each independently $C_{16}$-$C_{18}$ alkyl; $R_4$ is $-C_2H_2-$; x is 2; y is 1; n is 0; $L_1$ is–COOH, $-SO_3H$, or $-PO_3H_2$ and $L_2$ is absent or H.

**[0050]** The corrosion inhibitor can be a quaternary ammonium compound of Formula (IV):



$$R_1-\overset{\displaystyle R_2}{\underset{\displaystyle R_4}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R_3 \quad X^{\ominus}$$

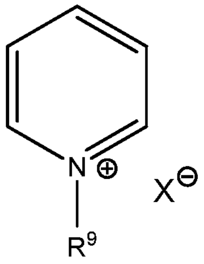
(IV)

wherein $R_1$, $R_2$, and $R_3$ are independently $C_1$ to $C_{20}$ alkyl, $R_4$ is methyl or benzyl, and $X^-$ is a halide or methosulfate.

**[0051]** Suitable alkyl, hydroxyalkyl, alkylaryl, arylalkyl or aryl amine quaternary salts include those alkylaryl, arylalkyl and aryl amine quaternary salts of the formula $[N^{+}R^{5a}R^{6a}R^{7a}R^{8a}][X^{-}]$ wherein $R^{5a}$, $R^{6a}$, $R^{7a}$, and $R^{8a}$ contain one to 18 carbon atoms, and X is Cl, Br or I. For the quaternary salts, $R^{5a}$, $R^{6a}$, $R^{7a}$, and $R^{8a}$ can each be independently selected from the group consisting of alkyl (e.g., $C_1$-$C_{18}$ alkyl), hydroxyalkyl (e.g., $C_1$-$C_{18}$ hydroxyalkyl), and arylalkyl (e.g., benzyl). The mono or polycyclic aromatic amine salt with an alkyl or alkylaryl halide include salts of the formula $[N^{+}R^{5a}R^{6a}R^{7a}R^{8a}][X^{-}]$ wherein $R^{5a}$, $R^{6a}$, $R^{7a}$, and $R^{8a}$ contain one to 18 carbon atoms and at least one aryl group, and X is Cl, Br or I.

**[0052]** Suitable quaternary ammonium salts include, but are not limited to, a tetramethyl ammonium salt, a tetraethyl ammonium salt, a tetrapropyl ammonium salt, a tetrabutyl ammonium salt, a tetrahexyl ammonium salt, a tetraoctyl ammonium salt, a benzyltrimethyl ammonium salt, a benzyltriethyl ammonium salt, a phenyltrimethyl ammonium salt, a phenyltriethyl ammonium salt, a cetyl benzyldimethyl ammonium salt, a hexadecyl trimethyl ammonium salt, a dimethyl alkyl benzyl quaternary ammonium salt, a monomethyl dialkyl benzyl quaternary ammonium salt, or a trialkyl benzyl quaternary ammonium salt, wherein the alkyl group has about 6 to about 24 carbon atoms, about 10 and about 18 carbon atoms, or about 12 to about 16 carbon atoms. The quaternary ammonium salt can be a benzyl trialkyl quaternary ammonium salt, a benzyl triethanolamine quaternary ammonium salt, or a benzyl dimethylaminoethanolamine quaternary ammonium salt.

**[0053]** The corrosion inhibitor component can comprise a pyridinium salt such as those represented by Formula (V):



(V)

wherein $R^9$ is an alkyl group, an aryl group, or an arylalkyl group, wherein said alkyl groups have from 1 to about 18 carbon atoms and $X^-$ is a halide such as chloride, bromide, or iodide. Among these compounds are alkyl pyridinium salts and alkyl pyridinium benzyl quats. Exemplary compounds include methyl pyridinium chloride, ethyl pyridinium chloride, propyl pyridinium chloride, butyl pyridinium chloride, octyl pyridinium chloride, decyl pyridinium chloride, lauryl pyridinium chloride, cetyl pyridinium chloride, benzyl pyridinium chloride and an alkyl benzyl pyridinium chloride, preferably wherein the alkyl is a $C_1$-$C_6$ hydrocarbyl group. Preferably, the pyridinium compound includes benzyl pyridinium chloride.

**[0054]** The corrosion inhibitor components can include additional corrosion inhibitors such as phosphate esters, monomeric or oligomeric fatty acids, or alkoxylated amines.

**[0055]** The corrosion inhibitor component can comprise a phosphate ester. Suitable mono-, di- and tri-alkyl as well as alkylaryl phosphate esters and phosphate esters of mono, di, and triethanolamine typically contain between from 1 to about 18 carbon atoms. Preferred mono-, di-and trialkyl phosphate esters, alkylaryl or arylalkyl phosphate esters are those prepared by reacting a $C_3$-$C_{18}$ aliphatic alcohol with phosphorous pentoxide. The phosphate intermediate interchanges its ester groups with triethylphosphate producing a more broad distribution of alkyl phosphate esters.

**[0056]** Alternatively, the phosphate ester can be made by admixing with an alkyl diester, a mixture of low molecular weight alkyl alcohols or diols. The low molecular weight alkyl alcohols or diols preferably include $C_6$ to $C_{10}$ alcohols or diols. Further, phosphate esters of polyols and their salts containing one or more 2-hydroxyethyl groups, and hydroxylamine phosphate esters obtained by reacting polyphosphoric acid or phosphorus pentoxide with hydroxylamines such as diethanolamine or triethanolamine are preferred.

**[0057]** The corrosion inhibitor component can include a monomeric or oligomeric fatty acid. Preferred monomeric or oligomeric fatty acids are $C_{14}$-$C_{22}$ saturated and unsaturated fatty acids as well as dimer, trimer and oligomer products obtained by polymerizing one or more of such fatty acids.

**[0058]** The corrosion inhibitor component can comprise an alkoxylated amine. The alkoxylated amine can be an ethoxylated alkyl amine. The alkoxylated amine can be ethoxylated tallow amine.

**[0059]** The component of the composition can comprise an organic sulfur compound, such as a mercaptoalkyl alcohol, mercaptoacetic acid, thioglycolic acid, 3,3'-dithiodipropionic acid, sodium thiosulfate, thiourea, L-cysteine, tert-butyl mercaptan, sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate, ammonium thiocyanate, sodium metabisulfite, or a combination thereof. Preferably, the mercaptoalkyl alcohol comprises 2-mercaptoethanol. The organic sulfur compound can constitute 0.5 to 15 wt. % of the composition, based on total weight of the composition, preferably about 1 to about 10 wt.% and more preferably about 1 to about 5 wt.%. The organic sulfur compound can constitute 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 wt. % of the composition.

**[0060]** The composition can be substantially free of or free of any organic sulfur compound other than the compound of formula (1). A composition is substantially free of any organic sulfur compound if it contains an amount of organic sulfur compound below the amount that will produce hydrogen sulfide gas upon storage at a temperature of 25°C and ambient pressure.

**[0061]** The component of the composition can further include a demulsifier. Preferably, the demulsifier comprises an oxyalkylate polymer, such as a polyalkylene glycol. The demulsifier can constitute from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of the composition, based on total weight of the composition. The demulsifier can constitute 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5 wt. % of the composition.

**[0062]** The component of the composition can include an asphaltene inhibitor. The composition can comprise from about 0.1 to 10 wt.%, from about 0.1 to 5 wt.%, or from about 0.5 to 4 wt.% of an asphaltene inhibitor, based on total weight of the composition. Suitable asphaltene inhibitors include, but are not limited to, aliphatic sulfonic acids; alkyl aryl sulfonic acids; aryl sulfonates; lignosulfonates; alkylphenol/aldehyde resins and similar sulfonated resins; polyolefin esters; polyolefin imides; polyolefin esters with alkyl, alkylenephenyl or alkylenepyridyl functional groups; polyolefin amides; polyolefin amides with alkyl, alkylenephenyl or alkylenepyridyl functional groups; polyolefin imides with alkyl, alkylenephenyl or alkylenepyridyl functional groups; alkenyl/vinyl pyrrolidone copolymers; graft polymers of polyolefins with maleic anhydride or vinyl imidazole; hyperbranched polyester amides; polyalkoxylated asphaltenes, amphoteric fatty acids, salts of alkyl succinates, sorbitan monooleate, and polyisobutylene succinic anhydride.

**[0063]** The component of the composition can include a paraffin inhibitor. The composition can comprise from about 0.1 to 10 wt.%, from about 0.1 to 5 wt.%, or from about 0.5 to 4 wt.% of an additional paraffin inhibitor, based on total weight of the composition. Suitable additional paraffin inhibitors include, but are not limited to, paraffin crystal modifiers, and dispersant/crystal modifier combinations. Suitable paraffin crystal modifiers include, but are not limited to, alkyl acrylate copolymers, alkyl acrylate vinylpyridine copolymers, ethylene vinyl acetate copolymers, maleic anhydride ester copolymers, branched polyethylenes, naphthalene, anthracene, microcrystalline wax and/or asphaltenes. Suitable paraffin dispersants include, but are not limited to, dodecyl benzene sulfonate, oxyalkylated alkylphenols, and oxyalkylated alkylphenolic resins.

**[0064]** The component of the composition can include a scale inhibitor. The composition can comprise from about 0.1 to 20 wt.%, from about 0.5 to 10 wt.%, or from about 1 to 10 wt.% of a scale inhibitor, based on total weight of the composition. Suitable scale inhibitors include, but are not limited to, phosphates, phosphate esters, phosphoric acids, phosphonates, phosphonic acids, polyacrylamides, salts of acrylamidomethyl propane sulfonate/acrylic acid copolymer (AMPS/AA), phosphinated maleic copolymer (PHOS/MA), and salts of a polymaleic acid/acrylic acid/acrylamidomethyl propane sulfonate terpolymer (PMA/AA/AMPS).

**[0065]** The component of the composition can include an emulsifier. The composition can comprise from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of an emulsifier, based on total weight of the composition. Suitable emulsifiers include, but are not limited to, salts of carboxylic acids, products of acylation reactions between carboxylic acids or carboxylic anhydrides and amines, and alkyl, acyl and amide derivatives of saccharides (alkyl-saccharide emulsifiers).

**[0066]** The component of the composition can include a water clarifier. The composition can comprise from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of a water clarifier, based on total weight of the composition. Suitable water clarifiers include, but are not limited to, inorganic metal salts such as alum, aluminum chloride, and aluminum chlorohydrate, or organic polymers such as acrylic acid based polymers, acrylamide based polymers, polymerized amines, alkanolamines, thiocarbamates, and cationic polymers such as diallyldimethylammonium chloride (DADMAC).

**[0067]** The component of the composition can include a dispersant. The composition can comprise from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of a dispersant, based on total weight of the composition. Suitable dispersants include, but are not limited to, aliphatic phosphonic acids with 2-50 carbons, such as hydroxyethyl diphosphonic acid, and aminoalkyl phosphonic acids, e.g. polyaminomethylene phosphonates with 2-10 N atoms e.g. each bearing at least one methylene phosphonic acid group; examples of the latter are ethylenediamine tetra(methylene phosphonate), diethylenetriamine penta(methylene phosphonate), and the triamine- and tetramine-polymethylene phosphonates with 2-4 methylene groups between each N atom, at least 2 of the numbers of methylene groups in each phosphonate being different. Other suitable dispersion agents include lignin, or derivatives of lignin such as lignosulfonate and naphthalene sulfonic acid and derivatives.

**[0068]** The component of the composition can include an emulsion breaker. The composition can comprise from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of an emulsion breaker, based on total weight of the composition. Suitable emulsion breakers include, but are not limited to, dodecylbenzylsulfonic acid (DDBSA), the sodium salt of xylenesulfonic acid (NAXSA), epoxylated and propoxylated compounds, anionic, cationic and nonionic surfactants, and resins, such as phenolic and epoxide resins.

**[0069]** The component of the composition can include an additional hydrogen sulfide scavenger. The composition can comprise from about 1 to 50 wt.%, from about 1 to 40 wt. %, or from about 1 to 30 wt. % of a hydrogen sulfide scavenger, based on total weight of the composition. Suitable additional hydrogen sulfide scavengers include, but are not limited to, oxidants (e.g., inorganic peroxides such as sodium peroxide or chlorine dioxide); aldehydes (e.g., of 1-10 carbons such as formaldehyde, glyoxal, glutaraldehyde, acrolein, or methacrolein; triazines (e.g., monoethanolamine triazine, monomethylamine triazine, and triazines from multiple amines or mixtures thereof); condensation products of secondary or tertiary amines and aldehydes, and condensation products of alkyl alcohols and aldehydes.

**[0070]** The component of the composition can include a gas hydrate inhibitor. The composition can comprise from about 0.1 to 25 wt.%, from about 0.1 to 20 wt. %, or from about 0.3 to 20 wt. % of a gas hydrate inhibitor, based on total weight of the composition. Suitable gas hydrate inhibitors include, but are not limited to, thermodynamic hydrate inhibitors (THI), kinetic hydrate inhibitors (KHI), and anti-agglomerates (AA). Suitable thermodynamic hydrate inhibitors include, but are not limited to, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, sodium bromide, formate brines (e.g. potassium formate), polyols (such as glucose, sucrose, fructose, maltose, lactose, gluconate, monoethylene glycol, diethylene glycol, triethylene glycol, mono-propylene glycol, dipropylene glycol, tripropylene glycols, tetrapropylene glycol, monobutylene glycol, dibutylene glycol, tributylene glycol, glycerol, diglycerol, triglycerol, and sugar alcohols (e.g. sorbitol, mannitol)), methanol, propanol, ethanol, glycol ethers (such as diethyleneglycol monomethylether, ethyleneglycol monobutylether), and alkyl or cyclic esters of alcohols (such as ethyl lactate, butyl lactate, methylethyl benzoate).

**[0071]** The component of the composition can include a kinetic hydrate inhibitor. The composition can comprise from about 5 to 30 wt.%, from about 5 to 25 wt. %, or from about 10 to 25 wt. % of a kinetic hydrate inhibitor, based on total weight of the composition. Suitable kinetic hydrate inhibitors and anti-agglomerates include, but are not limited to, polymers and copolymers, polysaccharides (such as hydroxyethylcellulose (HEC), carboxymethylcellulose (CMC), starch, starch derivatives, and xanthan), lactams (such as polyvinylcaprolactam, polyvinyl lactam), pyrrolidones (such as polyvinyl pyrrolidone of various molecular weights), surfactants (such as fatty acid salts, ethoxylated alcohols, propoxylated alcohols, sorbitan esters, ethoxylated sorbitan esters, polyglycerol esters of fatty acids, alkyl glucosides, alkyl polyglucosides, alkyl sulfates, alkyl sulfonates, alkyl ester sulfonates, alkyl aromatic sulfonates, alkyl betaine, alkyl amido betaines), hydrocarbon based dispersants (such as lignosulfonates, iminodisuccinates, polyaspartates), amino acids, and proteins.

**[0072]** The component of the composition can include a biocide. The composition can comprise from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of a biocide, based on total weight of the composition. Suitable biocides include, but are not limited to, oxidizing and non-oxidizing biocides. Suitable non-oxidizing biocides include, for example, aldehydes (e.g., formaldehyde, glutaraldehyde, and acrolein), amine-type compounds (e.g., quaternary amine compounds and cocodiamine), halogenated compounds (e.g., 2-bromo-2-nitropropane-3-diol (Bronopol) and 2-2-dibromo-3-nitrilopropionamide (DBNPA)), sulfur compounds (e.g., isothiazolone, carbamates, and metronidazole), and quaternary phosphonium salts (e.g., tetrakis(hydroxymethyl)-phosphonium sulfate (THPS)). Suitable oxidizing biocides include, for example, sodium hypochlorite, trichloroisocyanuric acids, dichloroisocyanuric acid, calcium hypochlorite, lithium hypochlorite, chlorinated hydantoins, stabilized sodium hypobromite, activated sodium bromide, brominated hydantoins, chlorine dioxide, ozone, and peroxides.

**[0073]** The component of the composition can include a pH modifier. The composition can comprise from about 0.1 to 20 wt.%, from about 0.5 to 10 wt.%, or from about 0.5 to 5 wt.% of a pH modifier, based on total weight of the composition. Suitable pH modifiers include, but are not limited to, alkali hydroxides, alkali carbonates, alkali bicarbonates, alkaline earth metal hydroxides, alkaline earth metal carbonates, alkaline earth metal bicarbonates and mixtures or combinations thereof. Exemplary pH modifiers include sodium hydroxide, potassium hydroxide, calcium hydroxide, calcium oxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, magnesium oxide, and magnesium hydroxide.

**[0074]** The component of the composition can include a surfactant. The composition can comprise from about 0.1 to 10 wt.%, from about 0.5 to 5 wt.%, or from about 0.5 to 4 wt.% of a surfactant, based on total weight of the composition. Suitable surfactants include, but are not limited to, anionic surfactants and nonionic surfactants. Anionic surfactants include alkyl aryl sulfonates, olefin sulfonates, paraffin sulfonates, alcohol sulfates, alcohol ether sulfates, alkyl carboxylates and alkyl ether carboxylates, and alkyl and ethoxylated alkyl phosphate esters, and mono and dialkyl sulfosuccinates and sulfosuccinamates. Nonionic surfactants include alcohol alkoxylates, alkylphenol alkoxylates, block copolymers of ethylene, propylene and butylene oxides, alkyl dimethyl amine oxides, alkyl-bis(2-hydroxyethyl) amine oxides, alkyl amidopropyl dimethyl amine oxides, alkylamidopropyl-bis(2-hydroxyethyl) amine oxides, alkyl polyglucosides, polyalkoxylated glycerides, sorbitan esters and polyalkoxylated sorbitan esters, and alkoyl polyethylene glycol esters and diesters. Also included are betaines and sultanes, amphoteric surfactants such as alkyl amphoacetates and amphodiacetates, alkyl amphopropionates and amphodipropionates, and alkyliminodipropionate.

**[0075]** Scavenger compositions made according to the invention can further include additional functional agents or additives that provide a beneficial property. For example, additional agents or additives can be sequestrants, solubilizers, lubricants, buffers, cleaning agents, rinse aids, preservatives, binders, thickeners or other viscosity modifiers, processing aids, carriers, water-conditioning agents, foam inhibitors or foam generators, threshold agents or systems, aesthetic enhancing agents (i.e., dyes, odorants, perfumes), or other additives suitable for formulation with a corrosion inhibitor composition, and mixtures thereof. Additional agents or additives will vary according to the particular corrosion inhibitor composition being manufactured and it's intend use as one skilled in the art will appreciate.

**[0076]** Alternatively, the compositions can not contain any of the additional agents or additives.

**[0077]** Additionally, the scavenger compositions can be formulated into a treatment fluid comprising the following components. These formulations include the ranges of the components listed and can optionally include additional agents.

| Component | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Scavenger composition | 30-90 | 30-90 | 30-90 | 30-90 | 30-90 | 30-90 | 65-85 | 65-85 | 65-85 | 65-85 | 65-85 | 30-90 |
| Organic solvent | 10-35 |  |  |  |  |  | 10-35 |  |  |  |  | 10-35 |
| Corrosion inhibitor | 0.1-20 | 0.1-20 |  |  |  |  | 0.1-20 | 0.1-20 |  |  |  | 0.1-20 |
| Asphaltene inhibitor | 0.1-5 | 0.1-5 | 0.1-5 | 0.1-5 |  |  | 0.1-5 | 0.1-5 | 0.1-5 |  |  | 0.1-5 |
| Paraffin inhibitor |  |  |  |  |  |  |  |  |  |  |  |  |
| Scale inhibitor | 1-10 | 1-10 | 1-10 | 1-10 | 1-10 |  | 1-10 | 1-10 | 1-10 | 1-10 |  | 1-10 |
| Emulsifier |  |  |  |  |  |  |  |  |  |  |  |  |
| Water clarifier |  |  |  |  |  |  |  |  |  |  |  |  |
| Dispersant |  |  |  |  |  |  |  |  |  |  |  |  |
| Emulsion breaker |  |  |  |  |  |  |  |  |  |  |  |  |
| Gas hydrate inhibitor |  |  |  |  |  |  |  |  |  |  |  | 0.1-25 |
| Biocide | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 |  |
| pH modifier |  |  |  |  |  |  |  |  |  |  |  |  |
| Surfactant |  |  |  |  |  |  |  |  |  |  |  |  |

| **Component** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** | **23** | **24** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Scavenger composition | 30-90 | 30-90 | 30-90 | 30-90 | 30-90 | 30-90 | 65-85 | 65-85 | 65-85 | 65-85 | 65-85 | 65-85 |
| Organic solvent | | | | | | | | | | | | |
| Corrosion inhibitor | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 | 0.1-20 |
| Asphaltene inhibitor | 0.1-5 | | | | | | 0.1-5 | | | | | |
| Paraffin inhibitor | | | | | | | | | | | | |
| Scale inhibitor | 1-10 | 1-10 | | | 1-10 | | 1-10 | 1-10 | | | | 1-10 |
| Emulsifier | | | | | | | | | | | | |
| Water clarifier | | | | | | | | | | | | |
| Dispersant | | | | | | | | | | | | |
| Emulsion breaker | | | | | | | | | | | | |
| Gas hydrate inhibitor | 0.1-25 | 0.1-25 | 0.1-25 | | | | 0.1-25 | 0.1-25 | 0.1-25 | | 0.1-25 | |
| Biocide | | | | | | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | 0.5-5 | | |
| pH modifier | | | | | | | | | | | | |
| Surfactant | | | | | | | | | | | | |

**[0078]** The term "formaldehyde" means formaldehyde, formalin, and/or paraformaldehyde.

**[0079]** “Hydrocarbon-containing fluid” means a liquid, gas, or mixture thereof that predominantly comprises aliphatic and/or aromatic hydrocarbons. The hydrocarbon-containing fluid may be crude, partially refined, or fully refined. The hydrocarbon-containing fluid of the present invention includes, but is not limited to, natural gas, crude oil, field oil, fuel oil, naphtha, gasoline, kerosene, diesel, slurry oil, gas oil, resid, refinery gas, coal gas, tar, asphalt, coke gas, ammonia synthesis gas, gas from a sulfurization plant, or an industrial gas stream.

**[0080]** Having described the invention in detail, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

## EXAMPLES

**[0081]** The following non-limiting examples are provided to further illustrate the present invention.

### Example 1: General Synthesis of Amine-Formaldehyde Compositions

**[0082]** An amine (2.89 moles) was added to a round bottom flask. Water (20-80 wt.% of the total composition) was added to the flask over the course of 30 minutes, causing the reaction temperature to increase to 57 °C. After allowing the reaction mixture to cool to 50 °C, formalin (5.04 moles) was added dropwise into the reaction mixture. The rate of formalin addition was adjusted to keep the reaction temperature between 50 °C and 66 °C. Once the addition was complete, the reaction mixture was stirred for 1 hour at 60-90 °C.

**[0083]** Other amine-formaldehyde formulations and their corresponding physical appearance are listed in Table 1.

Table 1.

| Entry | Amine | Formaldehyde source (formaldehyde/amine) | Results |
|---|---|---|---|
| 1 | Diethylenetriamine | Formalin (1.75:1) | Liquid product |
| 2 | Diethylenetriamine | Formalin (2:1) | Gelation turned to liquid after addition of IPA |
| 3 | Diethylenetriamine | Formalin (2.5:1) | Gelation turned to liquid after addition of IPA |
|  | Diethylenetriamine | Formalin (3.14:1) | Gelation turned to liquid after addition of IPA |
| 4 | Diethylenetriamine | Paraformaldehyde (1.5:1) | Liquid product |
| 5 | Diethylenetriamine | Paraformaldehyde (1.75:1) | Liquid product |
| 6 | Triethylenepentamine | Formalin (1.75:1) | Liquid product |
| 7 | Triethylenepentamine | Formalin (2:1) | Gelation |
| 8 | Triethylenepentamine | Formalin (3.14:1) | Gelation turned to liquid after addition of IPA |
| 9 | Triethylenepentamine | Formalin (4.75:1) | Gelation turned to liquid after addition of IPA |

**[0084]** A surfactant can be added to the reaction mixture to comprise 1-5 % (w/w) of the final solution, after the reaction mixture is allowed to cool to 45 °C. Formulations with a surfactant are listed in Table 2.

Table 2.

| Entry | Surfactant | Weight percent | Results |
|---|---|---|---|
| 1 | Trialkylamine oxide | 5 | Increase in reaction rate |
| 2 | Tetraalkylammonium chloride | 5 | Increase in reaction rate |
| 3 | Tetraalkylammonium sulfate | 5 | Increase in reaction rate |
| 4 | Ethyoxylated alkylalcohol | 5 | No effect on reaction |

Example 2: Performance Testing of Scavenging Compounds

**[0085]** To evaluate the scavenging properties of the compositions synthesized and formulated blends, each compound's scavenging efficiencies was investigated using a modified version of the ASTM D5705 vapor phase "Can Test" method typically employed in the Petroleum and Refining Industry to determine $H_2S$ and mercaptan concentrations above a confined sour hydrocarbon before and after chemical addition. $H_2S$ detector tubes are available for a wide range of concentrations. Likewise, mercaptan detector tubes are designed to detect and measure methyl, ethyl and isopropyl mercaptans simultaneously without distinguishing among the mercaptans contaminating the odiferous hydrocarbon.

**[0086]** Quart metal or glass cans were filled with 500 mL of sour hydrocarbon media (e.g., LVN or kerosene) and quickly capped to ensure $H_2S$ or mercaptans did not escape. Each sample was heated for a predetermined time in a hot water bath approximating refinery process and storage temperatures when possible. After the heating cycle had elapsed, the can was shaken to ensure that volatile compounds were in the vapor space of each can, and the vapor headspace concentrations of mercaptans or hydrogen sulfide were determined using detector tubes for the appropriate analyte. Samples were treated with the scavenging compound of interest and then heated in the hot water bath for a second heating cycle for a specified residence time at a specified temperature. Once the second heating cycle had elapsed, reductions in hydrogen sulfide and/or mercaptan concentrations were determined. The method allowed for product evaluation and determination of scavenging efficiencies for each scavenging compound.

**[0087]** A two hour residence time after addition of the scavenging compounds to sour kerosene while maintaining the temperature at 212 °F (100 °C) was used to test the compounds as reported in Table 3. Samples were treated at a dose ratio of 0.40 ppm scavenger per 1 ppm detected in the vapor space of each sample. Test compounds were compared to an incumbent (a promoted triazine based compound, commercially available from Nalco Champion, identified as IA hereinafter).

Table 3.

| Sample No. | Treatment | Dose (ppm) | Initial $H_2S$ (ppm) | Final $H_2S$ (ppm) | Amount $H_2S$ Reduced (ppm) | Percent Reduced | Dose Ratio |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0 | 1000 | 1000 | 0 | 0 | |
| 2 | Formaldehyde-diethylenetriamine | 400 | 1000 | 400 | 600 | 60 | 0.4:1 |
| 3 | Formaldehyde-tetrathylene-pentamine | 400 | 1000 | 400 | 600 | 60 | 0.4:1 |
| 4 | Formaldehyde-diethylenetriamine-alkylammonium chloride | 400 | 1000 | 50 | 950 | 95 | 0.4:1<br>5w/w% |
| 5 | Formaldehyde-tetrathylenepenta-amine-alkylammonium chloride | 400 | 1000 | 50 | 950 | 95 | 0.4:1<br>5w/w% |
| 6 | IA | 400 | 1000 | 200 | 800 | 80 | 0.4 |

**[0088]** These results are also visually depicted in Figure 1.

**[0089]** A two hour residence time after addition of the scavenging compounds to sour kerosene while maintaining the temperature at 212 °F (100 °C) was used to test the compounds as reported in Table 4. Samples were treated at a dose ratio of 0.80 ppm scavenger per 1 ppm detected in the vapor space of each sample. Test compounds were compared to two incumbents (IA and glyoxal, commercially available from Nalco Champion as Product ED5496A, identified as IB hereinafter).

Table 4.

| Sample No. | Treatment | Dose (ppm) | Initial $H_2S$ (ppm) | Final $H_2S$ (ppm) | Amount $H_2S$ Reduced (ppm) | Percent Reduced | Dose Ratio |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0 | 94000 | 94000 | 0 | 0 | |
| 2 | Formaldehyde-diethylenetriamine | 75000 | 94000 | 2000 | 92000 | 98 | 0.8:1 |
| 3 | IB | 75000 | 94000 | 79500 | 14500 | 15 | 0.8:1 |
| 4 | Formaldehyde-diethylenetriamine-alkylammonium chloride | 75000 | 94000 | 50 | 93950 | 99 | 0.8:1<br>5w/w% |
| 5 | IA | 75000 | 94000 | 50 | 93950 | 99 | 0.8:1 |

**[0090]** These results are also visually depicted in Figure 2.

**[0091]** A two hour residence time after addition of the scavenging compounds to sour kerosene while maintaining the temperature at 122 °F (50 °C) was used to test the compounds as reported in Table 5. Samples were treated at a dose ratio of 0.40 ppm scavenger per 1 ppm detected in the vapor space of each sample. Test compounds were compared to an incumbent (a glyoxal based compound, commercially available from Nalco Champion, identified as IC hereinafter).

Table 5.

| Sample No. | Treatment | Dose (ppm) | Initial $H_2S$ (ppm) | Final $H_2S$ (ppm) | Amount $H_2S$ Reduced (ppm) | Percent Reduced | Dose Ratio |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0 | 900 | 900 | 0 | 0 | |
| 2 | Formaldehyde-diethylenetriamine | 360 | 900 | 600 | 300 | 33 | 0.4:1 |
| 3 | Formaldehyde-diethylenetriamine-quaternary ammonium chloride | 360 | 900 | 5 | 895 | 99 | 0.4:1<br>5w/w% |
| 4 | Formaldehyde-diethylenetriamine-cocalkylamine oxides | 360 | 900 | 200 | 600 | 67 | 0.4:1<br>5w/w% |
| 5 | Formaldehyde-diethylenetriamine-Ethoxylated fatty alcohol | 360 | 900 | 500 | 400 | 55 | 0.4:1<br>5w/w% |
| 6 | IC | 360 | 900 | 400 | 500 | 44 | 0.4:1 |

**[0092]** A two hour residence time after addition of the scavenging compounds to sour kerosene while maintaining the temperature at approximately 75 °F (24 °C) was used to test the dosage of diethylenetriamine/formaldehyde (1:1.75) formulated with and without a surfactant at 5%w/w (tetraalkyl ammonium chloride).

Table 6.

| Sample No. | Treatment | Dose (ppm) | Initial $H_2S$ (ppm) | Final $H_2S$ (ppm) | Amount $H_2S$ reduced (ppm) | Percent reduced | Dose ratio |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0 | 800 | 800 | 0 | 0 | 0 |
| 2 | Formaldehyde-diethylenetriamine | 160 | 800 | 700 | 100 | 12.5 | 0.2:1 |
| 3 | Formaldehyde-diethylenetriamine | 320 | 800 | 700 | 100 | 12.5 | 0.4:1 |
| 4 | Formaldehyde-diethylenetriamine-alkylammonium chloride | 160 | 800 | 100 | 700 | 87.5 | 0.2:1 |
| 5 | Formaldehyde-diethylenetriamine-alkylammonium chloride | 320 | 800 | 2 | 798 | 99.75 | 0.4:1 |

**[0093]** Results are visually depicted in Figure 3.

**[0094]** A two hour residence time after addition of the scavenging compounds to sour unfinished fuel oil while maintaining the temperature at 212 °F (100 °C) was used to test the compounds as reported in Table 6. Samples were treated at a dose ratio of 0.40 ppm scavenger per 1 ppm detected in the vapor space of each sample. Test compounds were compared to an incumbent (1,3,5-trimethyl trimethylenetriamine, commercially available from Nalco Champion, identified as ID hereinafter).

Table 7.

| Sample No. | Treatment | Dose (ppm) | Initial $H_2S$ (ppm) | Final $H_2S$ (ppm) | Amount $H_2S$ Reduced (ppm) | Percent Reduced | Dose Ratio |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0 | 1000 | 900 | 0 | 0 | |
| 2 | Formaldehyde-diethylenetriamine | 400 | 1000 | 400 | 600 | 60 | 0.4:1 |
| 3 | Formaldehyde-tetraethylenepentamine-quaternary ammonium chloride | 400 | 1000 | 400 | 600 | 60 | 0.4:1<br>5w/w% |
| 4 | Formaldehyde-tetraethylenepentamine-cocalkylamine oxides | 400 | 1000 | 50 | 950 | 95 | 0.4:1<br>5w/w% |
| 5 | Formaldehyde-tetraethylenepentamine-Ethoxylated fatty alcohol | 400 | 1000 | 50 | 950 | 95 | 0.4:1<br>5w/w% |
| 6 | ID | 400 | 1000 | 200 | 800 | 80 | 0.4:1 |

**[0095]** When introducing elements of the present invention or the preferred embodiments(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

**[0096]** In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

**[0097]** As various changes could be made in the above products and methods without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

WHAT IS CLAIMED IS:

1. A method of reducing the amount of hydrogen sulfide or mercaptans in a hydrocarbon-containing fluid, the method comprising contacting an effective amount of a scavenger composition with the hydrocarbon-containing fluid, the scavenger composition comprising a surfactant and a reaction product of a polyamine and formaldehyde.

2. Use of a scavenger composition for reducing the amount of hydrogen sulfide or mercaptans in a hydrocarbon-containing fluid comprising contacting an effective amount of a scavenger composition with the hydrocarbon-containing fluid, the scavenger composition comprising a surfactant and a reaction product of a polyamine and formaldehyde.

3. The method or use of claim 1 or 2, wherein the hydrocarbon-containing fluid comprises crude oil, field oil, asphalt, naphtha, gasoline, kerosene, diesel, natural gas, refinery gas, coal gas, coke gas, ammonia synthesis gas, gas from a sulfurization plant, or an industrial gas stream.

4. The method or use of any one of claims 1 to 3, wherein the hydrocarbon-containing fluid is crude oil.

5. The method or use of any one of claims 1 to 4, wherein the polyamine comprises ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, tetrabutylenepentamine, hexaethyleneheptamine, hexapentyleneheptamine, heptaethyleneoctamine, octaethylenenonamine, nonaethylenedecamine, decaethyleneundecamine, decahexyleneundecamine, undecaethylenedodecamine, dodecaethylenetridecamine, tridecaethylenetetradecamine, N-tallow propylenediamine, or a combination thereof.

6. The method or use of claim 5, wherein the polyamine comprises diethylenetriamine, tetraethylenepentamine, or a combination thereof.

7. The method or use any one of claims 1 to 6, wherein the reaction product has a molar ratio of formaldehyde to polyamine of 0.1:1 to 25:1

8. The method or use of claim 7, wherein the reaction product has a molar ratio of formaldehyde to polyamine of 0.4:1 to 2:1.

9. The method or use of any one of claims 1 to 8, wherein the surfactant comprises a quaternary ammonium compound, a trialkylamine oxide, or a combination thereof.

10. The method or use of claim 9, wherein the surfactant comprises a tetraalkyl ammonium chloride, a tetraalkyl ammonium sulfate, a ($C_8$-$C_{20}$alkyl)di($C_1$-$C_4$alkyl) amine oxide, ethoxylated $C_4$-$C_{14}$ alcohol, or a combination thereof.

11. The method or use of claim 9, wherein the surfactant comprises tetralkyl ammonium chloride.

12. The method or use of any one of claims 1 to 11, wherein the surfactant is added to the scavenger composition at a concentration of from about 1 to about 10 wt.%, based on the total weight of the scavenger composition.

13. The method or use of claim 12, wherein the surfactant is added to the scavenger composition at a concentration of from about 1 to about 5 wt.%, based on the total weight of the scavenger composition.

14. The method or use of claim 12, wherein the surfactant is added to the scavenger composition at a concentration of from about 4 to about 6 wt.%, based on the total weight of the scavenger composition.

15. The method or use of any one of claims 1 to 14, wherein the scavenger composition is contacted with the hydrocarbon-containing fluid at a concentration from 0.2 to 0.8 ppm per 1 ppm of hydrogen sulfide or mercaptan detected in the vapor space of the hydrocarbon-containing fluid.

16. The method or use of claim 15, wherein the scavenger composition is contacted with the hydrocarbon-containing fluid at a concentration from 0.4 to 0.8 ppm per 1 ppm of hydrogen sulfide or mercaptan detected in the vapor space of the hydrocarbon-containing fluid.

17. The method or use of any one of claims 1 to 16, wherein the scavenger composition is contacted with the hydrocarbon-containing fluid at a temperature from about 20 °C to about 290 °C.

18. The method or use of claim 17, wherein the scavenger composition is contacted with the hydrocarbon-containing fluid at a temperature from about 20 °C to about 100 °C.

19. The method or use of any one of claims 1 to 18, wherein the rate of reaction between the hydrogen sulfide or mercaptan and the reaction product of a polyamine and formaldehyde is increased using the scavenger composition as compared to the rate of reaction using the reaction product of a polyamine and formaldehyde in the absence of the surfactant.

20. The method or use of claim 19, wherein the increased rate of reaction is demonstrated by a reduction in the hydrogen sulfide or mercaptan concentration of 2, 3, 4, 5, 6, 7, 8, or more times during a residence time of 2 hours at 100°C.

21. The method or use of claim 19, wherein the increased rate of reaction is demonstrated by a reduction in the hydrogen sulfide or mercaptan concentration of 8, or more times during a residence time of 2 hours at 100°C.

Figure 1

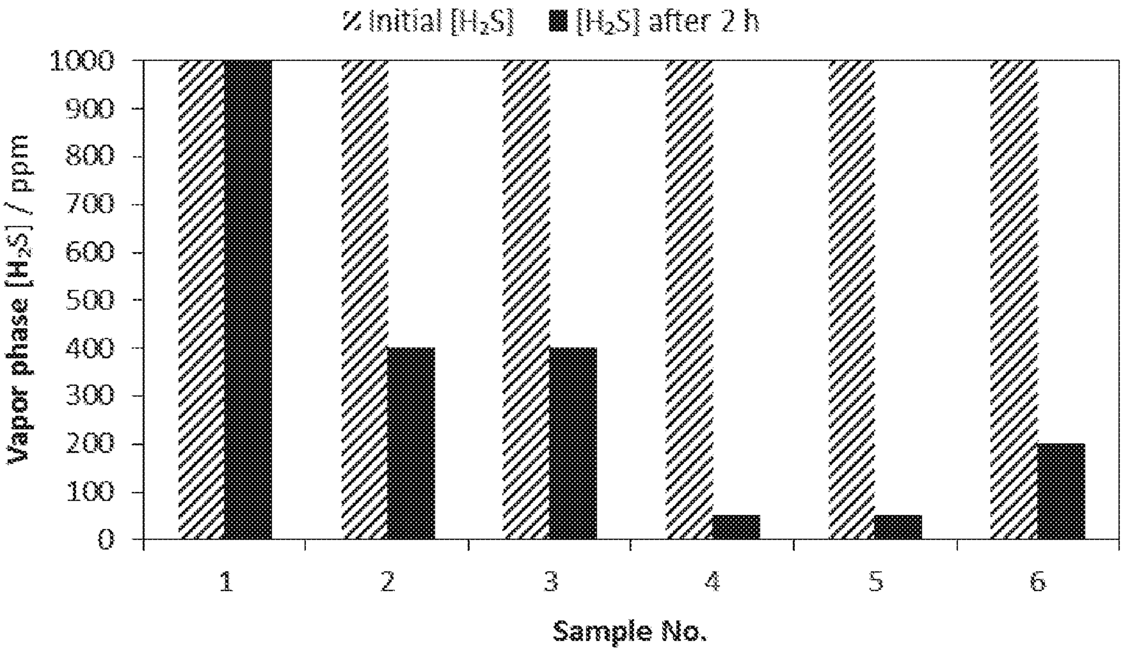

▨ Initial [H₂S]
■ [H₂S] after 2 h
Vapor phase [H₂S] / ppm
1000
900
800
700
600
500
400
300
200
100
0
1
2
3
4
5
6
Sample No.

Figure 2

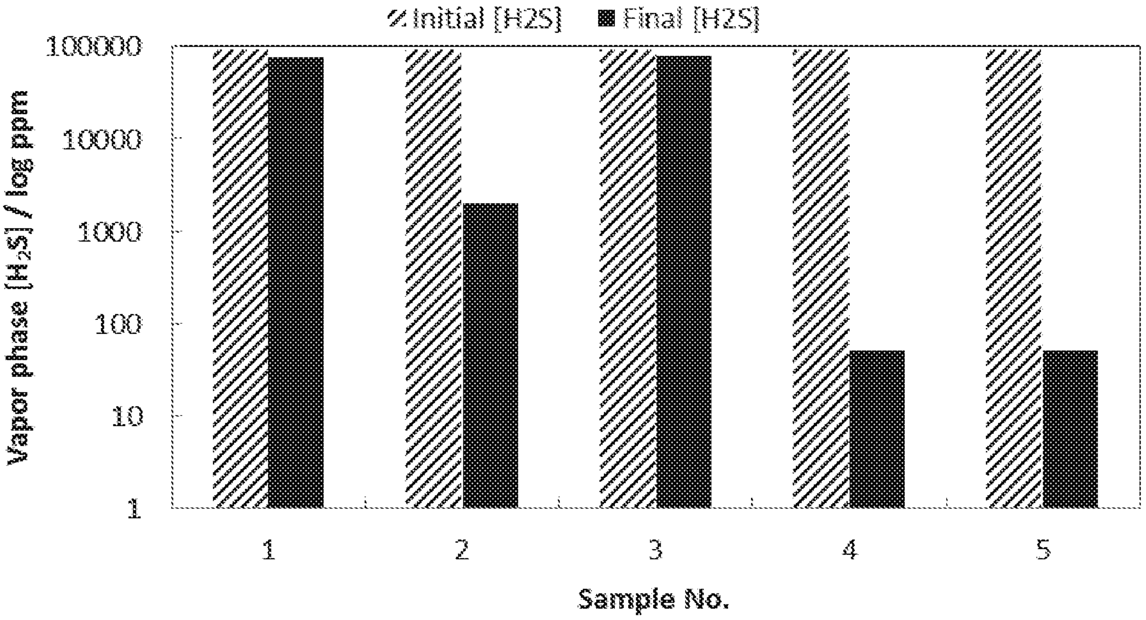
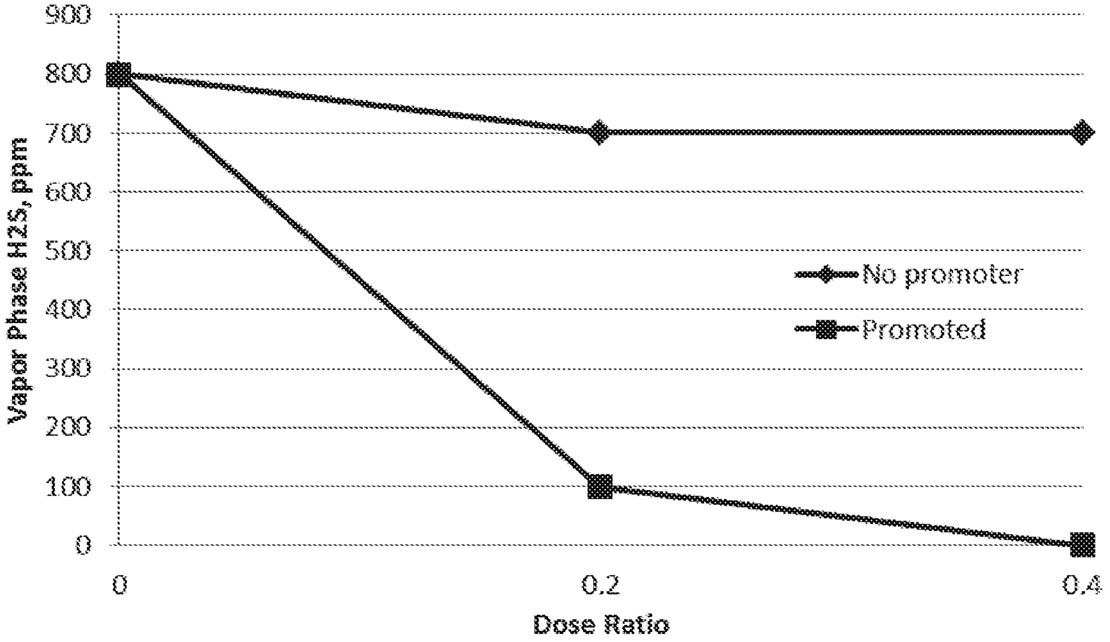

Initial [H2S]
Final [H2S]
100000
10000
1000
100
10
1
Vapor phase [$H_2S$] / log ppm
1
2
3
4
5
Sample No.

Figure 3


900
800
700
600
500
400
300
200
100
0
Vapor Phase H2S, ppm
0
0.2
0.4
Dose Ratio
No promoter
Promoted

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/033520

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G29/20
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

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

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

EPO-Internal, COMPENDEX, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>17 July 2017 | Date of mailing of the international search report<br>28/07/2017 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Van der Poel, Wim |

1

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