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(54) **Title:** REVERSE EMULSION BREAKER POLYMERS

(57) **Abstract:** The present invention generally relates to methods for resolving water and oil emulsions in the produced fluid of an oil production system comprising adding a reverse emulsion breaker to the produced fluid of the crude oil production system in an amount effective for resolving an oil-in-water emulsion. In particular, these methods for resolving an oil-in-water emulsion can be used in separation processes where the oil and solids in the produced fluid are separated from the produced water in the produced fluid.



REVERSE EMULSION BREAKER POLYMERS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Patent Application Serial No. 62/129,197 filed on March 6, 2015, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention generally relates to methods for resolving water and oil emulsions in the produced fluids of an oil production system comprising adding a reverse emulsion breaker to the produced fluid of the crude oil production system in an amount effective for resolving an oil-in-water emulsion. In particular, these methods for resolving an oil-in-water emulsion can be used in separation processes where the oil and solids in the produced fluid are separated from the produced water in the produced fluid.

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BACKGROUND OF THE INVENTION

[0003] Oil-in-water and water-in-oil-in-water emulsions can occur in many industrial systems. For example, these emulsions are a problem in many energy extraction systems because the produced fluids contain oil and solids dispersed in the produced water and separation of the oil and solids from the water is needed to comply with the oil sales specifications and to provide acceptable specifications before the water can be disposed of or re-used.

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[0004] In particular, oil-in-water and water-in-oil-in-water emulsions can be problems in produced fluid (steam assisted gravity drainage (SAGD), steam flood, etc.) separation processes where the oil and solids in the produced fluid are separated from the produced water in the produced fluid.

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[0005] For example, SAGD operations inject steam into geological formations to stimulate the production of bitumen or heavy hydrocarbon. Oil sands deposits in Alberta, Canada represent an area where this process is extensively used. Pairs of horizontal wells are bored into the oil-containing formation. The upper well injects steam and the lower well which is positioned below the steam injection line, continuously extracts a complex emulsion. That emulsion contains bitumen and water. The emulsion is broken; the bitumen is sent for upgrading/refining, while the produced water (separated from the emulsion) is treated and reused as feedwater for the steam generators.

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SUMMARY OF THE INVENTION

[0006] One aspect of the invention is a method of resolving a reverse emulsion in produced fluid of an oil production system comprising adding a reverse emulsion breaker to the produced fluid of the crude oil production system in an amount effective for
5 resolving the reverse emulsion, wherein the reverse emulsion breaker is a polyquaternary ammonium salt. The polyquaternary ammonium salt comprises the reaction product of contacting a polyamine intermediate with either a difunctional alkylating agent or a crosslinking agent. The polyamine intermediate comprises a reaction product of
10 contacting (i) a diamine, a triamine, a tetramine, or a combination thereof with (ii) urea, a dicarboxylic acid, an acid anhydride, a dialkyl ester of a carboxylic acid, or a combination thereof.

[0007] Other objects and features will be in part apparent and in part pointed out hereinafter.

15 BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a schematic of a separation system to separate solids, oil, and water in an emulsified hydrocarbon fluid.

[0009] Corresponding reference characters indicate corresponding parts throughout the drawings.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] The present invention is directed to methods for the improved separation of water and oil in oil production and processing operations. The method of the present invention comprises treating a system containing oil and water, where emulsions form,
25 with a polyquaternary ammonium salt solution. The polyquaternary ammonium salt containing treatments of the present invention were found to be effective treatments for resolving (breaking or inhibiting) oil-in-water (reverse) and water-in-oil-in-water emulsions in petroleum processes. Particularly, these reverse emulsion breakers are effective for improving the water quality in steam-assisted gravity drainage (SAGD)
30 processes. The reverse emulsion breakers disclosed herein are also typically water-soluble.

[0011] One aspect of the invention is a method of resolving a reverse emulsion in produced fluid of an oil production system comprising adding a reverse emulsion breaker to a produced fluid of the oil production system in an amount effective for resolving the

reverse emulsion, the reverse emulsion breaker comprising a polyquaternary ammonium salt.

[0012] Another aspect of the invention is a reverse emulsion breaker comprising a polyquaternary ammonium salt.

5 [0013] Yet another aspect of the invention is a reverse emulsion breaker comprising a reaction product of a polymerization mixture comprising polyquaternary ammonium salt.

[0014] Further, the reverse emulsion breaker described herein can be used in a method of resolving a reverse emulsion in produced fluids of an oil production system comprising adding the reverse emulsion breaker to the produced emulsion of the oil
10 production system in an amount effective for resolving the reverse emulsion.

[0015] The reverse emulsion can be an oil-in-water emulsion, a water-in-oil-in-water emulsion, or a combination thereof. Particularly, the reverse emulsion can be a water-in-oil-in-water emulsion.

15 [0016] For the reverse emulsion breaker described herein, the reverse emulsion breaker is a polyquaternary ammonium salt; the polyquaternary ammonium salt being the reaction product of contacting a polyamine intermediate with either a difunctional alkylating agent or a crosslinking agent; the polyamine intermediate being a reaction product of contacting (i) a diamine, a triamine, a tetramine, or a combination thereof, with
20 (ii) urea, a dicarboxylic acid, an acid anhydride, a dialkyl ester of a carboxylic acid, or a combination thereof.

[0017] The diamine, triamine, or tetramine can be dimethylaminopropylamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminobutylamine, dimethylaminopentylamine, dimethylaminohexylamine, dimethylaminoheptylamine, dimethylaminooctylamine, dimethylaminononylamine, dimethylaminodecylamine, dimethylaminolauryl amine, methyl bis(3-aminopropyl)amine, methyl bis(3-aminoethyl)amine, N-(2-aminoethyl)piperazine, dimethyltriethylenetetramine, diethylaminopropylamine, aminodiethylaminostearyl alcohol, N'-bis(propylaminoethyl)butylenediamine, bis(aminopropyl)propanediamine, aminotripropylamine, dimethylaminoallylamine, diethanolaminododecylamine, diethylenetriamine, triethylenetetramine, bis(hexamethylene)triamine, or a combination thereof.
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[0018] The diamine can comprise dimethylaminopropylamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminobutylamine,

dimethylaminopentylamine, or a combination thereof. Preferably, the diamine can comprise dimethylaminopropylamine.

[0019] The dicarboxylic acid can be a linear C₂-C₃₆ dicarboxylic acid, an anhydride thereof, a dialkyl ester thereof, or a combination thereof.

5 **[0020]** The dicarboxylic acid can be oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, fumaric acid, itaconic acid, citraconic acid, undecanedioic acid, dodecanedioic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, glutaconic acid, traumatic acid, muconic acid, brassic acid, brassylic acid, roccellic acid, tartaric acid, diphenic acid, or a
10 combination thereof.

[0021] The acid anhydride can be malonic anhydride, succinic anhydride, glutaric anhydride, adipic anhydride, pimelic anhydride, suberic anhydride, azelaic anhydride, sebacic anhydride, fumaric anhydride, itaconic anhydride, citraconic anhydride, undecanedioic anhydride, dodecanedioic anhydride, phthalic anhydride, maleic anhydride,
15 brassic anhydride, brassylic anhydride, roccellic anhydride, or a combination thereof.

[0022] The dialkyl ester of a carboxylic acid can be dimethyl malonate, diethyl malonate, dimethyl succinate, diethyl succinate, dimethyl glutarate, diethyl glutarate, dimethyl adipate, diethyl adipate, dimethyl pimelate, diethyl pimelate, dimethyl suberate, diethyl suberate, dimethyl azelate, diethyl azelate, dimethyl sebacate, diethyl sebacate,
20 dimethyl fumarate, diethyl fumarate, dimethyl itaconate, diethyl itaconate, dimethyl citraconate, diethyl citraconate, dimethyl undecanedioate, diethyl undecanedioate, dimethyl dodecanedioate, diethyl dodecanedioate, dimethyl phthalate, diethyl phthalate, dimethyl maleate, diethyl maleate, dimethyl brassate, diethyl brassate, dimethyl brassylate, diethyl brassylate, dimethyl roccellate, diethyl roccellate, or a combination thereof.

25 **[0023]** The dialkyl ester of a carboxylic acid can be dimethyl succinate, diethyl succinate, dimethyl malonate, diethyl malonate, dimethyl glutarate, diethyl glutarate, a dibasic ester thereof, or a combination thereof.

[0024] The polyamine intermediate can comprise a reaction product of contacting a diamine, a triamine, a tetramine, or a combination thereof with urea. The polyamine
30 intermediate can comprise a reaction product of dimethylaminopropylamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminobutylamine, dimethylaminopentylamine, or a combination thereof (preferably, dimethylaminopropylamine) with urea.

[0025] The polyamine intermediate can comprise a reaction product of contacting a diamine, a triamine, a tetramine, or a combination thereof with succinic anhydride. The polyamine intermediate can comprise a reaction product of dimethylaminopropylamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminobutylamine, 5 dimethylaminopentylamine, or a combination thereof (preferably, dimethylaminopropylamine) with succinic anhydride.

[0026] The polyamine intermediate can comprise a reaction product of contacting a diamine, a triamine, a tetramine, or a combination thereof with dimethyl malonate, diethyl malonate, malonic acid, or a combination thereof. The polyamine intermediate can 10 comprise a reaction product of dimethylaminopropylamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminobutylamine, dimethylaminopentylamine, or a combination thereof (preferably, dimethylaminopropylamine) with dimethyl malonate, diethyl malonate, malonic acid, or a combination thereof.

[0027] The polyamine intermediate can comprise a reaction product of contacting 15 diethylenetriamine, dipropylenetriamine, or bis(6-aminohexamethylene) amine with urea.

[0028] The polyquaternary ammonium salt can comprise a reaction product of the polyamine intermediate with a difunctional alkylating agent. The difunctional alkylating agent can be 1,3-dichloropropan-2-ol, bis(2-chloroethyl)ether, triglycoldichloride, difluoroisobutylether, dibromomethylether, diiododecylpolyether, dichlorononylpolyether, 20 difluorotetrabutyldecylpolyether, epichlorohydrin-functionalized polyethylene glycol, epichlorohydrin-functionalized polypropylene glycol, epichlorohydrin-functionalized poly(ethylene oxide-co-propylene oxide), bisphenol A diglycidyl ether, or a combination thereof.

[0029] The difunctional alkylating agent can comprise bis(2-chloroethyl)ether, 1,3- 25 dichloropropan-2-ol, or a combination thereof. The difunctional alkylating agent can comprise 1,3-dichloropropan-2-ol. The difunctional alkylating agent can comprise bis(2-chloroethyl)ether.

[0030] The difunctional alkylating agent can comprise epichlorohydrin-functionalized polyethylene glycol, epichlorohydrin-functionalized polypropylene glycol, 30 epichlorohydrin-functionalized poly(ethylene oxide-co-propylene oxide), or a combination thereof.

[0031] The polyquaternary ammonium salt can comprise a reaction product of the polyamine intermediate with a crosslinking agent. The crosslinking agent can be a

reaction product of epichlorohydrin and trimethylolpropane, glycerin, sorbitol, pentaerithritol, polypropylene glycol, polyethylene glycol, or a combination thereof.

[0032] The crosslinking agent can comprise a reaction product of epichlorohydrin and trimethylolpropane. Further, the crosslinking agent can comprise a reaction product
5 of epichlorohydrin and glycerin.

[0033] The crosslinking of the polyquaternary amine can be achieved by reacting a polyamine intermediate, diamine, triamine or tetramine with a difunctional alkylating agent or a crosslinking agent followed by reaction with difunctional alkylating agent, or a combination thereof.

10 **[0034]** The crosslinking agent can also be used to react with terminal chloromethylene groups of polyquaternary ammonium salts.

[0035] The crosslinking agent can be diethylenetriamine, polyethyleneimine, triethylenetetramine, tetraethylenepentamine, or a combination of thereof.

[0036] The reverse emulsion can be a water-in-oil-in-water emulsion.

15 **[0037]** The number average molecular weight of the polyquaternary ammonium salt can be from about 200 Daltons to about 200,000 Daltons, from about 200 Daltons to about 100,000 Daltons, from about 200 Daltons to about 80,000 Daltons, from about 200 Daltons to about 60,000 Daltons, from about 200 Daltons to about 40,000 Daltons, from about 1,000 Daltons to about 200,000 Daltons, from about 1,000 Daltons to about 100,000
20 Daltons, from about 1,000 Daltons to about 80,000 Daltons, from about 1,000 Daltons to about 60,000 Daltons, from about 1,000 Daltons to about 40,000 Daltons.

[0038] Preferably, the number average molecular weight of the polyquaternary ammonium salt can be from about 2,000 to about 20,000 Daltons.

[0039] The reverse emulsion breakers are typically water-soluble.

25 **[0040]** The produced water of the oil production system can be produced water from a steam-assisted gravity drainage production system or a cyclic steam stimulation system.

[0041] The produced water can be from a steam-assisted gravity drainage production system.

30 **[0042]** The effective amount of the reverse emulsion breaker can be from about 2 ppm to about 200 ppm, from about 2 ppm to about 180 ppm, from about 2 ppm to about 160 ppm, from about 2 ppm to about 150 ppm, from about 2 ppm to about 120 ppm, from about 2 ppm to about 100 ppm, from about 10 ppm to about 200 ppm, from about 10 ppm to about 180 ppm, from about 10 ppm to about 160 ppm, from about 10 ppm to about 150

ppm, from about 10 ppm to about 120 ppm, from about 10 ppm to about 100 ppm based on the total volume of the produced fluid.

[0043] Preferably, the effective amount of the reverse emulsion breaker can be from about 20 ppm to about 75 ppm based on the total volume of the produced fluid.

5 [0044] The reverse emulsion breaker can be combined with an emulsion breaker to the produced fluid of the oil production system.

[0045] The emulsion breaker can comprise an oxyalkylated phenol-formaldehyde resin, a resin ester, an oxyalkylated polyalkylamine, a polyol, a cross-linked polyol with a di- or multi-functional cross-linker, an isocyanate, an acid, or a combination thereof.

10 Preferably, the emulsion breaker can comprise a polyol and resin blend.

[0046] Preferably, the reverse emulsion breaker is water-soluble.

[0047] When the reverse emulsion breaker is used to break an emulsion in an oil production system, the emulsion can be in the produced fluid from a steam-assisted gravity drainage production system or a cyclic steam stimulation system.

15 [0048] Further, when the reverse emulsion breaker is used to break an emulsion in an oil production system, the produced fluid is from a steam-assisted gravity drainage production system.

[0049] In some instances, the emulsion breaker and the reverse emulsion breaker have a synergistic effect for resolving the water-in-oil-in-water emulsion in the produced water of an oil production system.

20 [0050] The emulsion breaker can have a concentration from about 1 ppm to about 2,000 ppm, from about 1 ppm to about 1,000 ppm, from about 1 ppm to about 750 ppm, from about 1 ppm to about 500 ppm, from about 10 ppm to about 2,000 ppm, from about 10 ppm to about 1,000 ppm, from about 10 ppm to about 750 ppm, from about 10 ppm to about 500 ppm, from about 50 ppm to about 2,000 ppm, from about 50 ppm to about 1,000 ppm, from about 50 ppm to about 750 ppm, from about 50 ppm to about 500 ppm, from about 100 ppm to about 2,000 ppm, from about 100 ppm to about 1,000 ppm, from about 100 ppm to about 750 ppm, or from about 100 ppm to about 500 ppm.

[0051] The reverse emulsion breaker can be used in combination with a flocculant.

30 [0052] A diluent can be added to the production system and the diluent can be condensate, naphtha, kerosene, light crude oil, or a combination thereof.

[0053] The polyquaternary ammonium salts of the present invention can be prepared by polycondensation of polyamine intermediate(s) with difunctional alkylating

agent or with the crosslinker/difunctional alkylating agent mixture or with the crosslinker followed by polycondensation with difunctional alkylating agent.

[0054] The reverse emulsion breaker can be dissolved in a solvent. The solvent can be water, methanol, ethylene glycol, or organic polar solvent.

5 **[0055]** The reverse emulsion breaker of the composition can further comprise a coagulant or a flocculant.

[0056] The coagulant can be a cationic polymer with a molecular weight ranging from about 500 Da to about 1,000,000 Da, from about 500 Da to about 500,000 Da, from about 500 Da to about 300,000 Da, from about 500 Da to about 100,000 Da, from about
10 3000 Da to about 1,000,000 Da, from about 3000 Da to about 500,000 Da, from about 3000 Da to about 300,000 Da, from about 3000 Da to about 100,000 Da, from about 10,000 Da to about 1,000,000 Da, from about 10,000 Da to about 500,000 Da, from about 10,000 Da to about 300,000 Da, from about 30,000 Da to about 1,000,000 Da, from about 30,000 Da to about 500,000 Da, or from about 30,000 Da to about 300,000 Da.

15 **[0057]** The flocculants can be a cationic polymer with a molecular weight ranging from about 200,000 Da to about 15,000,000 Da, from about 500,000 Da to about 15,000,000 Da, from about 1,000,000 Da to about 15,000,000 Da, from about 5,000,000 Da to about 15,000,000 Da, from about 10,000,000 Da to about 15,000,000 Da, from about 200,000 Da to about 12,000,000 Da, from about 500,000 Da to about 12,000,000
20 Da, from about 1,000,000 Da to about 12,000,000 Da, from about 5,000,000 Da to about 12,000,000 Da, or from about 10,000,000 Da to about 12,000,000 Da.

[0058] The reverse emulsion breakers of the present invention are preferably added to the inlet emulsion to a water and oil separating system. The water and oil separating system is depicted in Figure 1 and comprises a production well 1 that produced
25 a produced fluid carried in a produced fluid line 5. To the produced fluid line 5 can be added an emulsion breaker, a reverse emulsion breaker, or a combination thereof at injection point 10. When the reverse emulsion breaker is combined with the optional emulsion breaker, they can be injected independently, simultaneously, or sequentially. Further, a diluent can be injected at injection point 20. The produced fluid is then sent to
30 one or more separation vessels 30. The separation vessels can be a free water knock out (FWKO) vessel, a heat treater, or a phase separator. The produced water from the separation vessel(s) is carried in a produced water line 40 to a flotation tank 60. The produced water from the flotation tank 60 is sent to a skim tank 70 where the bottoms are sent to a produced water tank through the produced water tank line 90 and recycled oil is

skimmed from the surface of the liquid in the skim tank 70 and sent back to the produced fluid line 5 through the recycled oil line 80. The tops from the separation vessels are sent to the oil tank through the oil line 50.

5 **[0059]** The efficacy of the reverse emulsion breaker polyquaternary ammonium salt is dependent upon a number of factors such as water drop, water quality, interface quality, oil dryness, and the like.

10 **[0060]** Emulsion stability is monitored by measuring phase separation at about 90°C to about 150°C using conventional bottle testing. The produced emulsion (100 mL) is poured in a 6 ounce prescription glass bottle and heated for approximately 30 to 60 minutes at about 90°C to about 150°C in a water bath. A diluent is added to the emulsion and mixed using a mechanical shaker at low speed for five minutes or mixed by shaking the bottle by hand. In some tests the mixed emulsion is placed back in the water bath at about 90°C to about 150°C; in other cases the next step is injection. The reverse emulsion breaker (REB), and optionally emulsion breaker (EB) and are injected at a designated
15 dose, hand-shaken for 100 cycles (or in a shaker at low setting for 1 minute), and placed in the water bath at 90°C for observation of water drop during 60-120 minutes. Basic sediments and water (BS&W) are determined by diluting 6 mL of the oil close to the interface with 6 mL xylene, toluene, or mineral spirits (e.g., Varsol™) and centrifuging for five minutes. Water clarity was ranked on a comparative visual scale from 11 (partially
20 broken reverse) to a 1 (≤ 50 NTU). A rating of 9 could be deemed equivalent to 1500 NTU, while a rating of 4 or 5 would be equal to about 500 NTU.

25 **[0061]** 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

30 **[0062]** The following non-limiting examples are provided to further illustrate the present invention.

Example 1: Synthesis of crosslinkers based on glycerol

[0063] Glycerol (50.15 grams) and 0.4 mL of boron trifluoride diethyl etherate (47% BF₃ basis) were placed in a flask equipped with a stirrer, a thermometer, a

condenser, and an addition tube. This solution was heated to 60°C. Then, 453.16 grams of epichlorohydrin was added dropwise. The epichlorohydrin was added over a period of two hours; the temperature was kept between 60 to 70°C and controlled by external cooling. After the exothermic reaction was over, the temperature was raised to 65°C and an
5 additional 0.2 mL of boron trifluoride diethyl etherate was added. The reaction was continued for additional 2 to 3 hours to insure complete reaction.

Example 2: Synthesis of a polyamine intermediate 1

[0064] N, N-dimethylaminopropylamine (306.2 grams) was placed in a 500 mL
10 kettle reactor equipped with a condenser, an overhead stirrer, a thermocouple, an outlet to an aqueous hydrochloric acid bath (to neutralize ammonia released during reaction), and a nitrogen inlet. The amine was heated to 150°C. When the temperature was stabilized, 90.1 grams of urea was added portionwise (addition time from 30 minutes to 1 hour) with monitoring of the ammonia release rate. When the urea addition was finalized, the reaction
15 mixture was kept at 160°C for 16 hours. Then, the product was transferred to a bottle and analyzed.

Example 3: Synthesis of a polyquaternary ammonium salt

[0065] The polyamine intermediate prepared in Example 2 (100.6 g) was placed in
20 the flask equipped with a stirrer, a thermometer, a condenser, and an addition tube. The temperature was raised to 115°C. Then, 4.1 grams of the crosslinker prepared in Example 1 was weighed and added to polyamine intermediate. The reaction mixture was stirred at 115°C for 3 hours. Then, 41 grams of water was added followed by dropwise addition of 61.0 grams of bis(2-chloroethyl)ether. When the addition was finalized, an additional 30
25 grams of water was added and the reaction mixture was held at 115°C until the chloride content was about 9.5% and the quaternary amines content was higher than 95%. Then, the reaction mixture was transferred to a bottle and analyzed.

Example 4: Synthesis of crosslinked polyquaternary ammonium salt

[0066] The polyquaternary ammonium salt from Example 3 (100 grams) was
30 placed in the flask and heated to 115°C followed by addition of 1 gram of diethylenetriamine (E-100, PEI). The reaction mixture was kept at 115°C for 3 hours and then transferred to a bottle and analyzed.

Example 5: Synthesis of polyamine intermediate

[0067] Diethylenetriamine (355.35g) was placed in 1 L kettle reactor equipped with a condenser, an overhead stirrer, a thermocouple, an outlet to an aqueous hydrochloric acid bath (to neutralize ammonia released during reaction), and a nitrogen inlet. The amine was heated to 150°C. When the temperature was stabilized, 207.20 grams of urea was added portionwise (addition time from 30 minutes to 1 hour) with monitoring of ammonia release rate. When the urea addition was finalized, the reaction mixture was left to react at 160°C for 16 hours. Then, the product was transferred to a bottle and analyzed.

Example 6: Synthesis of Product 1

[0068] Polyamine intermediate prepared according to Example 2 (100 grams) and 45.0 grams of water were placed in the flask equipped with a stirrer, a thermometer, a condenser, and an addition tube. The temperature was raised to 200°F. Then, 56.0g of 1,3-dichloroisopropanol was added portionwise (addition time: 30-40 minutes). The reaction mixture was stirred at 115°C for 2 to 3 hours. Then, 30.0 grams of water and 0.3- 0.5 mL of 2-ethylhexanol were added and the reaction was kept at 115°C for 16-20 hours. The reaction was finalized by addition of 82 grams of water. The product was then transferred to a bottle and analyzed.

Example 7: Synthesis of Product 3

[0069] Dimethylaminopropylamine (204.36g) was placed in a flask equipped with an overhead stirrer, a thermocouple, a condenser, and a Dean-Stark trap. Diethyl malonate (160.17 grams or 132.15 grams of dimethyl malonate or 104.06 grams of malonic acid) and 1.65 grams of para-toluenesulfonic acid, monohydrate were added and the reaction mixture was heated to 240°F (115°C) until no by-product (ethanol in case of diethyl malonate, methanol in case of dimethyl malonate and water in case of malonic acid) was collected in the Dean-Stark trap and the tertiary amine content was greater than 98%. The intermediate wasn't purified or separated. The Dean-Stark trap was disconnected. Water (80.7 grams) was added and the mixture was heated to 104°C (220°F). Then, 143.01 grams of bis(2-chloroethyl)ether was added dropwise using an addition funnel. The addition rate was adjusted to control the exotherm generated during reaction. The reaction temperature was kept between 100–113°C (212–235°F). When the addition was finalized the reaction mixture was kept at 113°C (235°F) for 3 hours. Then, 121.01 grams of D.I.

water was added and the reaction mixture was heated at 113° (235°F) for 16 hours. The process was finalized when the quaternary ammonium salt content was higher than 90.00%. To stop the reaction and dilute the product, 201.7 grams of D.I. water was added. The final product was transferred to a bottle and analyzed.

- 5 **[0070]** Product 2 was synthesized using the procedure above, except succinic anhydride was substituted for the diethyl malonate and 1,3-dichloroisopropanol was substituted for bis(2-chloroethyl)ether.

Example 8: Synthesis of crosslinker

- 10 **[0071]** Poly(ethylene glycol) (300.15 grams) was placed in the flask equipped with a stirrer, a thermometer, a condenser, and an addition funnel. Boron trifluoride diethyl etherate (0.75 mL, 47% based on BF₃, Aldrich) was added and mixture was heated to 60°C. Then, 138.85 grams of epichlorohydrin was added dropwise over 1 hour. After the addition of epichlorohydrin was finalized, the temperature was raised to 75°C and reaction
15 mixture was kept at that temperature for 4 hours. The product was transferred to a storage container and used for further reaction.

Example 9: Synthesis of crosslinked polyquaternary amine

- [0072]** Product from Example 8 (57.36 grams), 30.68 grams of polyamine
20 intermediate as prepared in Example 2 and 20.22 grams of water were placed in the flask equipped with a stirrer, a thermometer, a condenser, and an addition tube. The temperature was raised to 115°C and the reaction mixture was kept at this temperature for 4 to 10 hours. Then, 8.43 grams of 1,3-dichloroisopropanol was added portion-wise to the reaction mixture (addition time of 30-40 minutes). The reaction mixture was stirred at 115°C for 2-
25 3 hours. Then, 29.0 grams of water and about 0.3 – 0.5 mL of 2-ethylhexanol were added. The reaction was kept at 115°C for 16-20 hours. Then, the reaction was kept at 115°C for 16-20 hours. The reaction was finalized by addition of 45.67 grams of water. The product was then transferred to a bottle and analyzed.

- 30 Example 10: Test results

[0073] Emulsion stability was monitored by measuring phase separation at about 90°C using conventional bottle testing. The produced emulsion (100 mL) was poured in a 6 ounce prescription glass bottle and heated for approximately 30 to 60 minutes at about 90°C in a water bath. A diluent (e.g., an aromatic solvent) was added to the emulsion and

mixed using a mechanical shaker at low speed for five minutes or mixed by shaking the bottle by hand. In some tests the mixed emulsion was placed back in the water bath at 90°C and in other cases the next step was injection of the reverse emulsion breaker and optionally, the emulsion breaker into the emulsion. The flow sheet of the production plant that is being mimicked determines whether the emulsion was placed back into the water bath or if the reverse emulsion breaker, and optionally, the emulsion breaker were injected into the emulsion.

[0074] An emulsion breaker (EB) and a reverse emulsion breaker (REB) were injected by syringe at a designated dose, shook by hand for 100 cycles, and placed in the water bath at 90°C for observation during 60-120 minutes. Basic sediments (BS = emulsion content in thief) and water (W = water content in thief) were determined by diluting 6 mL of the oil close to the interface with 6 mL xylene, toluene, or mineral spirits (e.g., Varsol™) and centrifuging for five minutes and BS + W is the sum of those measurements. Water clarity (WQ) was ranked on a comparative visual scale from 11 (partially broken reverse) to a 1 (≤ 50 NTU). A rating of 9 could be deemed equivalent to 1500 NTU, while a rating of 4 or 5 would be equal to about 500 NTU. Water drop (WD) was measured at 5, 15, and 30 minutes.

[0075] EB A, EB B, REB 1, REB 2, and REB 3 are incumbent products. The composition of Products 1-3 are detailed below.

Canada SAGD location 1: EB A (polyol/resin blend) at 380 ppm								
REB	Conc. (ppm)	WD (5 min.)	WD (15 min.)	WD (30 min.)	WQ	W	BS	W + BS
REB 1 (polyamine quat)	75	74	80	84	11	0.0	6.0	6.0
Product 1	75	80	84	87	10	0	3.2	3.2
Product 2	75	80	84	87	10	1.2	2	3.2
Product 3	75	80	80	82	7	1.2	1.2	2.4
REB 1 (polyamine quat)	100	60	68	80	6	0.4	4.8	5.2
Product 1	100	84	84	85	4	0	2.6	2.6
Product 2	100	84	84	88	5	1.2	1.6	2.8
Product 3	100	82	83	86	4	1.2	1.6	2.8
REB 1 (polyamine quat)	125	80	80	82	5	0.4	3.4	3.8
Product 1	125	84	87	88	3	0	2.4	2.4

Product 2	125	86	86	89	4	1.2	0.8	2
Product 3	125	85	86	89	3	0.8	1.6	2.4
REB 1 (polyamine quat)	150	76	80	82	4	1.2	3.4	4.6
Product 1	150	86	86	89	3	0	2	2
Product 2	150	84	86	87	3	1.2	0.8	2
Product 3	150	86	87	88	3	1	1.8	2.8

Canada SAGD location 2: EB B (oxyalkylated polyol blend) at 300 ppm					
REB	Conc. (ppm)	WD (2 min.)	WD (30 min.)	WQ (2 min.)	WQ (30 min.)
REB 2 (polyamine quat)	25	65	70	6	5
REB 3 (polyamine quat)	25	60	68	8	7
Product 3	25	68	70	6	5
REB 2 (polyamine quat)	30	69	73	6	5
REB 3 (polyamine quat)	30	60	70	8	8
Product 3	30	69	73	5	5
REB 2 (polyamine quat)	35	65	68	7	6
REB 3 (polyamine quat)	35	70	70	5	5
Product 3	35	70	71	5	5
REB 2 (polyamine quat)	40	70	73	5	4
REB 3 (polyamine quat)	40	70	72	6	6
Product 3	40	72	73	5	5

	Components	mass in reaction mix, g	Composition (%)
Product 1	N,N'-Bis[3-(dimethylamino)propyl]urea	101.03	32.2
Product 1	1,3-dichloroisopropanol	55.93	17.8

Product 1	water	157	50
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Int 2	N,N-dimethylpropylamine (DMPA)	185.13	
Int 2	Succinic Anhydride	90.66	
Int 2	p-TSA monohydrate	1.99	
Product 2	Int 2: (N,N'-Bis[3-(dimethylamino)propyl]-succinamide)	261.5	34.7
Product 2	1,3-dichloropropan-2-ol	115.3	15.3
Product 2	Water	376	50

Int 3	N,N-dimethylpropylamine (DMPA)	75.76	
Int 3	Diethyl malonate	59.36	
Product 3	Int 3: (N,N'-Bis[3-(dimethylamino)propyl]-malonamide)	101	32.2
Product 3	Bis(2-chloroethyl ether)	55.9	17.8
Product 3	water	157	50

[0076] When introducing elements of the present invention or the preferred embodiments 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.

[0077] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0078] As various changes could be made in the above compositions 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 resolving a reverse emulsion in produced fluid of an oil production system comprising adding a reverse emulsion breaker to the produced fluid of the crude oil production system in an amount effective for resolving the reverse emulsion, wherein the reverse emulsion breaker is a polyquaternary ammonium salt; the polyquaternary ammonium salt being the reaction product of contacting a polyamine intermediate with either a difunctional alkylating agent or a crosslinking agent; the polyamine intermediate being a reaction product of contacting (i) a diamine, a triamine, a tetramine, or a combination thereof with (ii) urea, a dicarboxylic acid, an acid anhydride, a dialkyl ester of a carboxylic acid or a combination thereof.

2. The method of claim 1 wherein the diamine, triamine, or tetramine is dimethylaminopropylamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminobutylamine, dimethylaminopentylamine, dimethylaminohexylamine, dimethylaminoheptylamine, dimethylaminooctylamine, dimethylaminononylamine, dimethylaminodecylamine, methylethylaminolauryl amine, methyl bis(3-aminopropyl)amine, methyl bis(3-aminoethyl)amine, N-(2-aminoethyl)piperazine, dimethyltriethylenetetramine, diethylaminopropylamine, aminodiethylaminostearyl alcohol, N'-bis(propylaminoethyl)butylenediamine, bis(aminopropyl)propanediamine, aminotripropylamine, dimethylaminoallylamine, diethanolaminododecylamine, diethylenetriamine, triethylenetetramine, bis(hexamethylene)triamine, or a combination thereof.

3. The method of claim 2 wherein the diamine comprises dimethylaminopropylamine.

4. The method of any one of claims 1 to 3 wherein the dicarboxylic acid is a linear C₂-C₃₆ dicarboxylic acid, their anhydrides, or a combination thereof.

5. The method of claim 4 wherein the dicarboxylic acid is oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, fumaric acid, itaconic acid, citraconic acid, undecanedioic acid, dodecanedioic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid,

glutaconic acid, traumatic acid, muconic acid, brassic acid, brassylic acid, roccellic acid, tartaric acid, diphenic acid, or a combination thereof.

6. The method of any one of claims 1 to 5 wherein the acid anhydride is malonic anhydride, succinic anhydride, glutaric anhydride, adipic anhydride, pimelic anhydride, suberic anhydride, azelaic anhydride, sebacic anhydride, fumaric anhydride, itaconic anhydride, citraconic anhydride, undecanedioic anhydride, dodecanedioic anhydride, phthalic anhydride, maleic anhydride, brassic anhydride, brassylic anhydride, roccellic anhydride, or a combination thereof.

7. The method of any one of claims 1 to 6 wherein the dialkyl ester of a carboxylic acid is dimethyl malonate, diethyl malonate, dimethyl succinate, diethyl succinate, dimethyl glutarate, diethyl glutarate, dimethyl adipate, diethyl adipate, dimethyl pimelate, diethyl pimelate, dimethyl suberate, diethyl suberate, dimethyl azelate, diethyl azelate, dimethyl sebacate, diethyl sebacate, dimethyl fumarate, diethyl fumarate, dimethyl itaconate, diethyl itaconate, dimethyl citraconate, diethyl citraconate, dimethyl undecanedioate, diethyl undecanedioate, dimethyl dodecanedioate, diethyl dodecanedioate, dimethyl phthalate, diethyl phthalate, dimethyl maleate, diethyl maleate, dimethyl brassate, diethyl brassate, dimethyl brassylate, diethyl brassylate, dimethyl roccellate, diethyl roccellate, or a combination thereof.

8. The method of any one of claims 1 to 7 wherein the dialkyl ester of a carboxylic acid is dimethyl succinate, diethyl succinate, dimethyl malonate, diethyl malonate, dimethyl glutarate, diethyl glutarate, a dibasic ester thereof, or a combination thereof.

9. The method of any one of claims 1 to 8 wherein the polyamine intermediate comprises a reaction product of contacting a diamine, a triamine, a tetramine, or a combination thereof with urea.

10. The method of any one of claims 1 to 8 wherein the polyamine intermediate comprises a reaction product of contacting a diamine, a triamine, a tetramine, or a combination thereof with succinic anhydride.

11. The method of any one of claims 1 to 8 wherein the polyamine intermediate comprises a reaction product of contacting a diamine, a triamine, a tetramine, or a combination thereof with dimethyl malonate, diethyl malonate, malonic acid, or a combination thereof.

12. The method of any one of claims 1 to 9 wherein the polyamine intermediate comprises a reaction product of contacting diethylenetriamine, dipropylenetriamine, or bis(6-aminohexamethylene) amine with urea.

13. The method of any one of claims 1 to 12 wherein the difunctional alkylating agent is 1,3-dichloropropan-2-ol, bis(2-chloroethyl)ether, triglycoldichloride, difluoroisobutylether, dibromomethylether, diiododecylpolyether, dichlorononylpolyether, difluorotetrabutyldecylpolyether, epichlorohydrin-functionalized polyethylene glycol, epichlorohydrin-functionalized polypropylene glycol, epichlorohydrin-functionalized poly(ethylene oxide-co-propylene oxide), bisphenol A diglycidyl ether, or a combination thereof.

14. The method of any one of claims 1 to 13 wherein the difunctional alkylating agent comprises bis(2-chloroethyl)ether.

15. The method of any one of claims 1 to 13 wherein the difunctional alkylating agent comprises 1,3-dichloropropan-2-ol.

16. The method of any one of claims 1 to 13 wherein the difunctional alkylating agent comprises epichlorohydrin-functionalized polyethylene glycol, epichlorohydrin-functionalized polypropylene glycol, epichlorohydrin-functionalized poly(ethylene oxide-co-propylene oxide), or a combination thereof.

17. The method of any one of claims 1 to 16 wherein the crosslinking agent is a reaction product of polyepichlorohydrin and trimethylolpropane, glycerin, sorbitol, pentaerithritol, polypropylene glycol, polyethylene glycol, or a combination thereof.

18. The method of any one of claim 1 to 17 wherein the crosslinking agent comprises a reaction product of polyepichlorohydrin and trimethylolpropane.

19. The method of any one of claim 1 to 17 wherein the crosslinking agent comprises a reaction product of polyepichlorohydrin and glycerin.
20. The method of any one of claims 1 to 19 wherein the crosslinking agent is used to react with terminal chloromethylene groups of polyquaternary ammonium salts.
21. The method of claim 20 wherein the crosslinking agent is diethylenetriamine, polyethyleneimine, triethylenetetramine, tetraethylenepentamine or a combination of thereof.
22. The method of any one of claims 1 to 21 wherein the reverse emulsion is a water-in-oil-in-water emulsion.
23. The method of any one of claims 1 to 22, wherein the molecular weight of the polyquaternary ammonium salt is from about 200 to about 200,000 Daltons.
24. The method of claim 23, wherein the molecular weight of the polyquaternary ammonium salt is from about 2,000 to about 20,000 Daltons.
25. The method of any one of claims 1 to 24 wherein the reverse emulsion breaker is water-soluble.
26. The method of any one of claims 1 to 25 wherein the produced water of the oil production system is produced water from a steam-assisted gravity drainage production system or a cyclic steam stimulation system.
27. The method of claim 26, wherein the produced water is from a steam-assisted gravity drainage production system.
28. The method of any one of claim 1 to 27 wherein the effective amount of the reverse emulsion breaker is from about 2 ppm to about 200 ppm based on the total volume of the produced fluid.

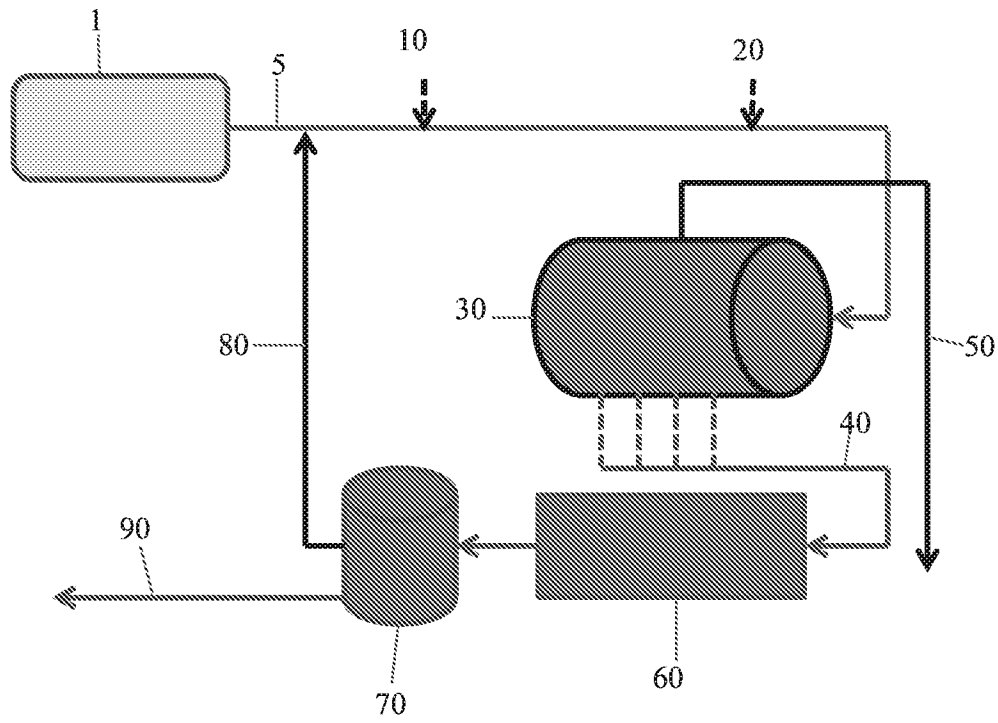
29. The method of claim 28 wherein the effective amount of the reverse emulsion breaker is from about 20 ppm to about 75 ppm based on the total volume of the produced fluid.

30. The method of any one of claims 1 to 29 further comprising adding an emulsion breaker to the produced fluid of the oil production system.

31. The method of claim 30 wherein the emulsion breaker comprises an oxyalkylated phenol-formaldehyde resin, a resin ester, an oxyalkylated polyalkylamine, a polyol, a cross-linked polyol with a di- or multi-functional cross-linker, an isocyanate, an acid, or a combination thereof.

32. The method of claim 31 wherein the emulsion breaker comprises a polyol and resin blend.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/020248

A. CLASSIFICATION OF SUBJECT MATTER IPC (2016.01) B01D 17/04, B01D 17/05 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) IPC (2016.01) B01D 17/04, B01D 17/05 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) Databases consulted: THOMSON INNOVATION, Google Patents, Google Scholar, PatBase Search terms used: polyamine, diamine, triamine, tetramine, emulsion, urea, quaternary ammonium		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3993615 A W. R. GRACE & CO 23 Nov 2000 (2000/11/23) the whole document	1-32
Y	US 4303780 A PETROLITE CORPORATION 01 Dec 1981 (1981/12/01) Column 1 lines 1 to 22	1-32
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 Jun 2016		Date of mailing of the international search report 14 Jun 2016
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616		Authorized officer TAIEB - SABO Hagit Telephone No. 972-2-5651612

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/020248

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
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		CA 1045286 A	26 Dec 1978
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