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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

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

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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. 62/128,326 filed on March 4, 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 as 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.

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 or re-used.

[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.

[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.

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 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 poly(triethanolamine) with an alkylating agent. The alkylating agent comprising a C_1-C_{12} alkyl halide, a C_1-C_{12} haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions, or a combination thereof.

[0007] Another aspect of the invention is a composition for resolving a reverse emulsion in produced fluid of an oil production system comprising an effective amount of a reverse emulsion breaker and an effective amount of an emulsion breaker, the reverse emulsion breaker comprising a polyquaternary ammonium salt. The polyquaternary ammonium salt comprising the reaction product of contacting a poly(triethanolamine) with an alkylating agent. The alkylating agent comprising a C_1-C_{12} alkyl halide, a C_1-C_{12} haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions, or a combination thereof.

[0008] Other objects and features will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1 is a schematic of a separation system to separate solids, oil, and water in an emulsified hydrocarbon fluid.

[0010] Corresponding reference characters indicate corresponding parts throughout the drawings.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] 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, with a polyquaternary ammonium salt solution. The polyquaternary ammonium-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) processes. The reverse emulsion breakers disclosed herein are also typically water-soluble.

[0012] 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 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 poly(triethanolamine) with an alkylating agent, the alkylating agent being a C_1-C_{12} alkyl halide, a C_1-C_{12} haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions, or a combination thereof.

[0013] Further, the invention is directed to a composition for resolving a reverse emulsion in produced fluid of an oil production system comprising an effective amount of a reverse emulsion breaker and an effective amount of an emulsion breaker, the reverse emulsion breaker being a polyquaternary ammonium salt, the polyquaternary ammonium salt being the reaction product of contacting a poly(triethanolamine) with an alkylating agent, the alkylating agent being a C_1-C_{12} alkyl halide, a C_1-C_{12} haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions, or a combination thereof.

[0014] For the methods and compositions herein, the alkylating agent can be 2-chloroethanol, ethyl chloride, propyl chloride, butyl chloride, glycidyl trimethylammonium chloride, 3-chloro-2-hydroxypropyltrimethylammonium chloride, benzyl chloride, or a combination thereof.

[0015] For the methods and compositions herein, the alkylene oxide is ethylene oxide, propylene oxide, butylene oxide, or a combination thereof and inorganic acid results in acidic conditions.

[0016] For the methods and compositions herein, the polyquaternary ammonium salt can comprise the reaction product of contacting a poly(triethanolamine) with ethylene oxide and an inorganic acid.

[0017] For the methods and compositions herein, the polyquaternary ammonium salt can comprise the reaction product of contacting a poly(triethanolamine) with 2-chloroethanol.

[0018] For the methods and compositions herein, the polyquaternary ammonium salt can comprise the reaction product of contacting a poly(triethanolamine) with 3-chloro-2-hydroxypropyltrimethylammonium chloride.

[0019] For the methods and compositions herein, the polyquaternary ammonium salt can comprise the reaction product of contacting a poly(triethanolamine) with benzyl chloride.

[0020] For the methods of resolving a reverse emulsion, the reverse emulsion can be a water-in-oil-in-water emulsion.

[0021] For the methods and compositions herein, the 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 50,000 Daltons, from about 1,000 Daltons to about 200,000 Daltons, from about 1,000 Daltons to about 100,000 Daltons, from about 1,000 Daltons to about 50,000 Daltons, or from about 1,000 Daltons to about 20,000 Daltons. Preferably, the molecular weight of the polyquaternary ammonium salt can be from about 2,000 Daltons to about 20,000 Daltons.

[0022] For the methods and compositions herein, the reverse emulsion breaker is water-soluble.

[0023] For the methods and compositions herein, the effective amount of the reverse emulsion breaker can be from about 2 ppm to about 200 ppm, from about 2 ppm to about 150 ppm, from about 2 ppm to about 100 ppm, from about 10 ppm to about 200 ppm, or from about 10 ppm to about 100 ppm, based on the total volume of the produced fluid. Preferably, 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.

[0024] The methods and compositions can further comprise adding an emulsion breaker to the produced fluid of the oil production system.

[0025] When the methods and compositions comprise an emulsion breaker, 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. Preferably, the emulsion breaker comprises a polyol and resin blend.

[0026] 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. Preferably, 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.

[0027] 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 fluid of an oil production system.

[0028] The emulsion breaker can have a concentration from about 100 ppm to about 500 ppm, from about 100 ppm to about 400 ppm, from about 100 ppm to about 300 ppm, or from about 100 ppm to about 200 ppm.

[0029] A diluent can be added to the production system and the diluent can be condensate, naphtha, kerosene, light crude oil, or a combination thereof.

[0030] The reverse emulsion breaker can be prepared in modification of polytriethanolamine using various alkyl halides, aryl halides, and the like.

[0031] The reverse emulsion breaker can be also prepared in reaction of polytriethanolamine with ethylene oxide under acidic conditions.

[0032] The reverse emulsion breaker can be dissolved in a solvent. The solvent can be water, methanol, ethylene glycol, propylene glycol.

[0033] 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 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 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.

[0034] The efficacy of the polyquaternary ammonium reverse emulsion breakers is dependent upon a number of factors such as water drop, water quality, interface quality, oil dryness, and the like.

[0035] 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 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 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.

[0036] 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

[0037] The following non-limiting examples are provided to further illustrate the present invention.

Example 1: Reaction of polytriethanolamine with ethylene oxide

[0038] Polytriethanolamine (600 grams) was placed in a glass bottle. Then, hydrochloric acid (550.0 grams, 36–38 wt.% in water) was added portionwise to bring the pH to less than 4. When the pH was stabilized, the sample was transferred to an autoclave and a gradual addition of ethylene oxide (mEO = 240g) at ambient temperature was started. The reaction was exothermic. After the addition was finalized, the reaction mixture was kept stirring for 10–16 hours at ambient temperature. The final product was

transferred to a bottle and analyzed. Product 1 was prepared as above and Product 2 was prepared as described using 331.92 g polytriethanolamine and 180 g ethylene oxide.

Example 2: Polytriethanolamine modified with 2-chloroethanol

[0039] Polytriethanolamine (250.94 gram) was placed in the round bottom flask and heated to 200°F (93.3°C). Then, 142.55 grams of 2-chloroethanol was added and the reaction mixture was heated to 200°F (93.3°C) and kept at this temperature for 3 hours. Then, 43.43 grams of water was added and the reaction mixture was kept at 200°F (93.3°C) for about 20 hours. The final product was transferred to a bottle and submitted for analysis (expected Cl%: 14.39%).

Example 3: Modification of pTEA with 3-chloro-2-hydroxypropyltrimethylammonium chloride

[0040] Modification of polytriethanolamine (pTEA) was performed as described in Example 2. The reaction temperature was set up at 200°F (93.3°C) and water was used as a solvent. The ratio of 3-chloro-2-hydroxypropyltrimethylammonium chloride to amine concentratoin of pTEA was varied from 1:4 to 1:1.

Example 4: Modification of pTEA with benzyl chloride

[0041] Modification of polytriethanolamine was again performed as described in Example 2. The reaction temperature was set up at 200°F (93.3°C) and water was used as a solvent. The ratio of benzyl chloride to amine concentration of pTEA was varied from 1:4 to 1:1.

Example 5: REB Test Results

[0042] 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 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. 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 and water (BS&W) 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. Water quality (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 a 5, 15, 30, 45, and 60 minutes. The emulsion breaker used was commercially available from Nalco Champion in Sugarland, TX as EC2512A and used at 350 ppm for the 90 ppm REB concentrations and at 380 ppm for the 100 ppm and 150 ppm REB concentrations.

REB	ppm	% Solvent	WD (5 min)	WD (15 min)	WD (30 min)	WD (45 min)	WD (60 min)	WQ
Product 1	90	25.0%	35	50	50	50	50	11
	100	25.0%	30	50	65	70	72	5
	150	25.0%	40	60	80	80	82	5
Product 2	90	25.0%	30	40	40	40	40	11
	100	25.0%	60	70	75	76	75	5
	150	25.0%	20	30	60	68	68	5

[0043] 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.

[0044] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0045] 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 poly(triethanolamine) with an alkylating agent,

the alkylating agent being a C_1-C_{12} alkyl halide, a C_1-C_{12} haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions, or a combination thereof.

2. The method of claim 1 wherein the alkylating agent is 2-chloroethanol, 3-chloro-2-hydroxypropyltrimethylammonium chloride, benzyl chloride, or a combination thereof.

3. The method of claim 1 wherein the alkylene oxide is ethylene oxide, propylene oxide, butylene oxide, or a combination thereof and an inorganic acid results in acidic conditions.

4. The method of claim 1 or 3 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with ethylene oxide and an inorganic acid.

5. The method of claim 1 or 2 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with 2-chloroethanol.

6. The method of claim 1 or 2 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with 3-chloro-2-hydroxypropyltrimethylammonium chloride.

7. The method of claim 1 or 2 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with benzyl chloride.

8. The method of any one of claims 1 to 7 wherein the reverse emulsion is a water-in-oil-in-water emulsion.

9. The method of any one of claims 1 to 8, wherein the molecular weight of the polyquaternary ammonium salt is from about 200 to about 200,000 Daltons.

10. The method of claim 9, wherein the molecular weight of the polyquaternary ammonium salt is from about 2,000 to about 20,000 Daltons.

11. The method of any one of claims 1 to 10 wherein the reverse emulsion breaker is water-soluble.

12. The method of any one of claims 1 to 11 wherein the produced fluid of the oil production system is produced fluid from a steam-assisted gravity drainage production system or a cyclic steam stimulation system.

13. The method of claim 12, wherein the produced fluid is from a steam-assisted gravity drainage production system.

14. The method of any one of claim 1 to 13 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.

15. The method of claim 14 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.

16. The method of any one of claims 1 to 15 further comprising adding an emulsion breaker to the produced fluid of the oil production system.

17. The method of claim 16 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.

18. The method of claim 17 wherein the emulsion breaker comprises a polyol and resin blend.

19. A composition for resolving a reverse emulsion in produced fluid of an oil production system comprising an effective amount of a reverse emulsion breaker and an effective amount of an emulsion breaker,

the reverse emulsion breaker being a polyquaternary ammonium salt,

the polyquaternary ammonium salt being the reaction product of contacting a poly(triethanolamine) with an alkylating agent,

the alkylating agent being a C_1-C_{12} alkyl halide, a C_1-C_{12} haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions, or a combination thereof.

20. The composition of claim 19 wherein the alkylating agent is ethylene oxide, 2-chloroethanol, 3-chloro-2-hydroxypropyltrimethylammonium chloride, benzyl chloride, or a combination thereof.

21. The composition of claim 19 or 20 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with ethylene oxide.

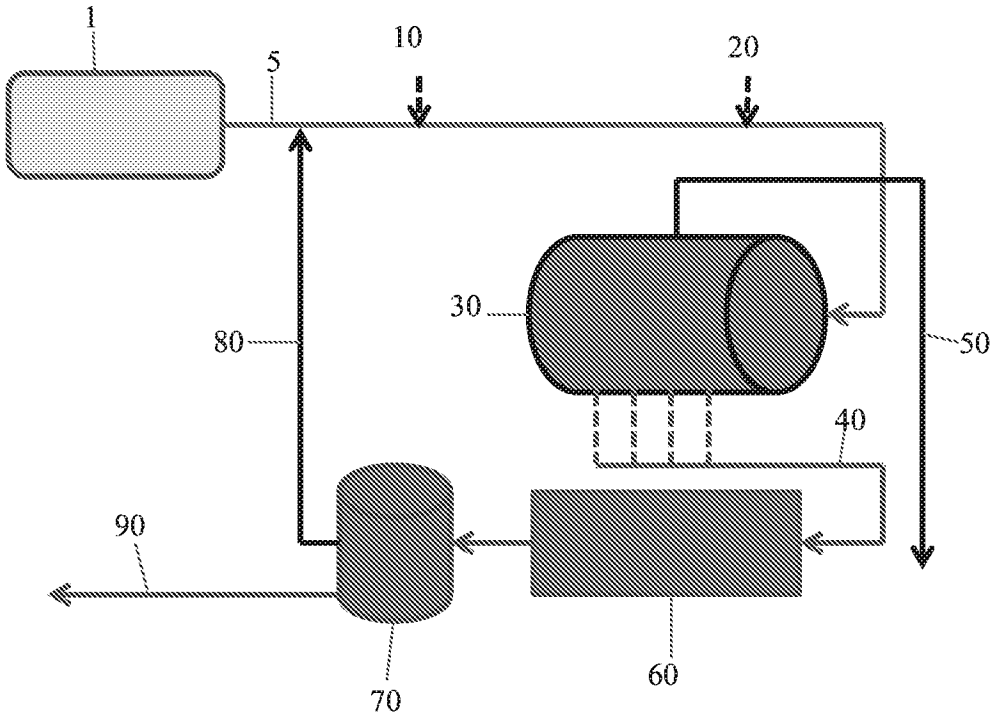
22. The composition of claim 19 or 20 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with 2-chloroethanol.

23. The composition of claim 19 or 20 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with 3-chloro-2-hydroxypropyltrimethylammonium chloride.

24. The composition of claim 19 or 20 wherein the polyquaternary ammonium salt comprises the reaction product of contacting a poly(triethanolamine) with benzyl chloride.

25. The composition of claim any one of claims 19 to 24 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.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/020439

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 Scholar, PatBase
Search terms used: Polytriethanolamine, quaternary ammonium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4505839 A PETROLITE CORPORATION 19 Mar 1985 (1985/03/19) Column 3 lines 41 to 48, Column 7 lines 58 to 61, table II, Claims 1,2	1-25
X	Becker.J. R. Crude Oil Waxes, Emulsions, and Asphaltenes.Tulsa, Oklahoma: PennWell Publishing Company, 1997, ISBN 0-87814-737-3. Becker.J. R 31 Dec 1997 (1997/12/31) pages 3, 84 to 85, Fig. 5-1.	19-25

☐ 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
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"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
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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA:	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

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Patent document cited search report	Publication date	Patent family member(s)	Publication Date
US 4505839 A	19 Mar 1985	US 4505839 A	19 Mar 1985
		US 4731481 A	15 Mar 1988
		US 4840748 A	20 Jun 1989