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(54) Title: METHOD AND COMPOSITION FOR ENHANCED OIL RECOVERY USING PHOSPHORUS-TAGGED SURFACTANTS

(57) Abstract: A method of enhanced oil recovery wherein: (a) a novel flooding composition is delivered into a subterranean reservoir; (b) the flooding composition includes a traceable surfactant having at least one traceable phosphorus moiety; and (c) the fluid produced from the subterranean reservoir is analyzed to determine if the traceable surfactant is present in the fluid. The traceable surfactant preferably includes a phosphate moiety, a phosphonate moiety, or a phosphinate moiety. The presence of the traceable surfactant in the fluid produced from the subterranean reservoir is preferably determined by digestion or titration.



METHOD AND COMPOSITION FOR ENHANCED OIL RECOVERY USING PHOSPHORUS-TAGGED SURFACTANTS

Related Case

5 [0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/786,660 filed on March 15, 2013 and incorporates said provisional application by reference into this document as if fully set out at this point.

Field of the Invention

10 [0002] The present invention relates to methods and compositions for enhanced oil recovery using traceable surfactants.

Background of the Invention

15 [0003] A need exists for improved reservoir flooding methods and compositions for enhanced oil recovery. In particular, a need exists for such improved methods and compositions which can be used to: (1) detect the presence of the flood surfactant in the flood front; (2) determine when the surfactant front of the flooding composition has arrived at the producing wells; (3) better analyze and understand the geology of the reservoir during trials, the location of injection wells, etc.; (4) detect and quantify the adsorption of the flooding surfactant on the formation rock; (5) understand other phenomena occurring in the reservoir during enhanced oil recovery; and (6) optimize final commercial flooding operations and other enhanced oil recovery procedures performed in the reservoir.

Summary of the Invention

25 [0004] The present invention provides a method, a composition, and traceable phosphorus-tagged surfactants for enhanced oil recovery which satisfy the needs and alleviate the problems discussed above.

30 [0005] In one aspect, there is provided an inventive method of enhanced oil recovery from a subterranean reservoir comprising the steps of: (a) delivering the inventive flooding composition into the subterranean reservoir, the flooding composition including a traceable surfactant having at least one traceable phosphorus moiety and (b) analyzing a fluid produced from the subterranean reservoir to determine if the traceable surfactant is present in the fluid.

 [0006] Examples of preferred traceable phosphorus moieties include phosphate moieties, phosphonate moieties, phosphinate moieties, or combinations thereof. Further, to determine the presence of the traceable surfactant in the fluid produced from the

subterranean reservoir, the fluid is preferably analyzed in a step (b) of the inventive method by digestion, titration, or other instrumentation capable of analyzing for phosphorous (e.g., ICP-OES, etc.)

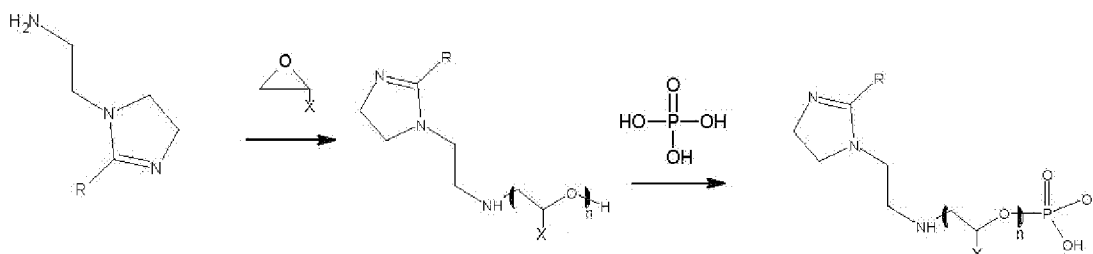
[0007] Further aspects, features, and advantages of the present invention will be apparent to those of ordinary skill in the art upon reading the following Detailed Description of the Preferred Embodiments.

Detailed Description of the Preferred Embodiments

[0008] The present invention provides a method, flooding composition, and traceable phosphorus-tagged surfactants for enhanced oil recovery from a subterranean reservoir. The inventive flooding composition includes one or more of the traceable phosphorus-tagged surfactant compounds. The inventive method preferably comprises the steps of delivering the flooding composition into the subterranean reservoir and then analyzing the fluid produced from the subterranean reservoir to determine if the traceable surfactant is present in the produced fluid.

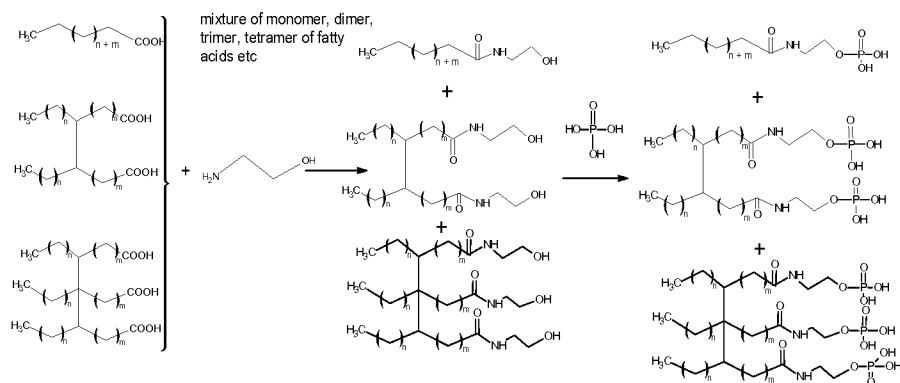
[0009] Examples of traceable surfactant materials suitable for use in the inventive flooding composition include, but are not limited to, compounds having one or more phosphate moieties, one or more phosphonate moieties, one or more phosphinate moieties, or a combination thereof. By way of example, but not by way of limitation, such surfactants can be prepared by reacting fatty alcohols or amines (linear or branched) with phosphites or phosphates to form phosphate, phosphonate, or phosphinate compounds. Alternatively, ethoxylated and/or propoxylated fatty alcohols or amines can be reacted with phosphites or phosphates to form phosphate, phosphonate, or phosphinate compounds.

[0010] Examples of traceable surfactant compounds preferred for use in the inventive flooding composition include, but are not limited to, surfactants which exhibit Winsor Type III phase behavior in the presence of a given oil and brine system. An example of one such tagged surfactant can be prepared in accordance with the following reaction formula:



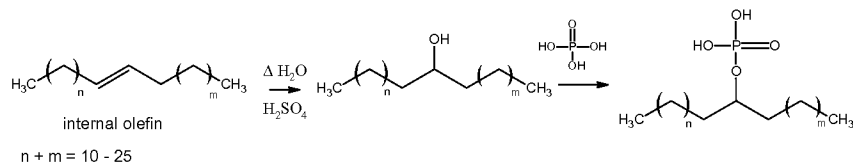
wherein: R will preferably be a linear or branched hydrocarbon constituent group having from about 8 to about 24 carbon atoms; X is hydrogen or a methyl group; and n is a value of from 1 to 12. In one embodiment, X is a methyl group and n is a value of from 1 to 5.

[0011] An example of another preferred traceable surfactant can be prepared in accordance with the following reaction formula:



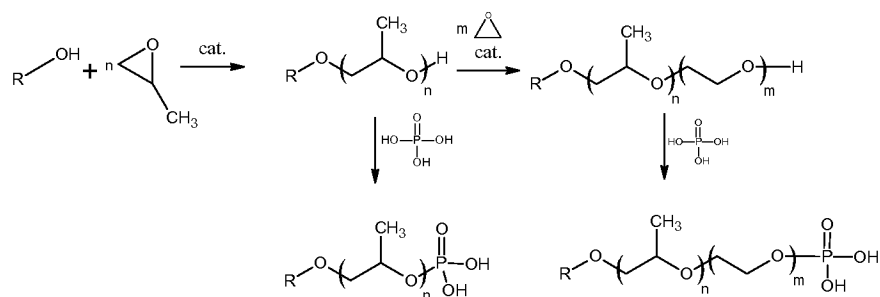
wherein the sum of $n + m$ is preferably in the range of from about 10 to about 22 and wherein the fatty acid reactant or reactant mixture preferably comprises from about 50% to 100% by weight dimer molecules and from 0% to about 50% trimer molecules. The molecule chain constituents can be linked by cyclohexane rings, single bonds etc.

[0012] Another preferred traceable surfactant can be prepared in accordance with the following reaction formula:



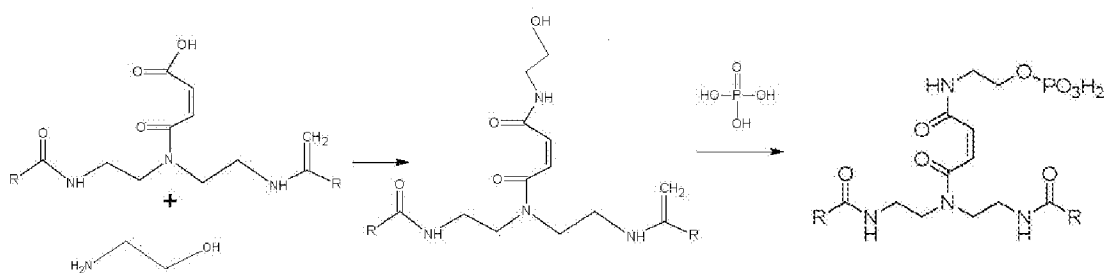
wherein the sum of $n + m$ is preferably in the range of from about 10 to about 25.

[0013] Two additional preferred traceable surfactants can be prepared as follows:



wherein R will preferably be a linear or branched hydrocarbon constituent group having from about 8 to about 30 (more preferably from about 10 to about 15) carbon atoms; n will preferably be in the range of from 0 to about 100, more preferably from about 2 to about 15; and m will preferably be in a range of from 0 to about 100, more preferably from about 2 to about 15.

[0014] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:

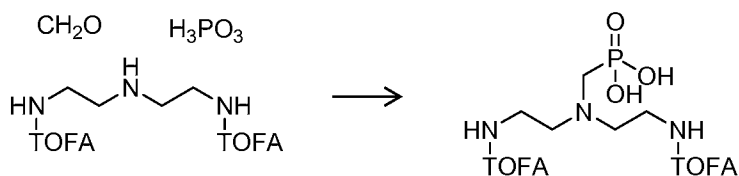


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phosphoric acid

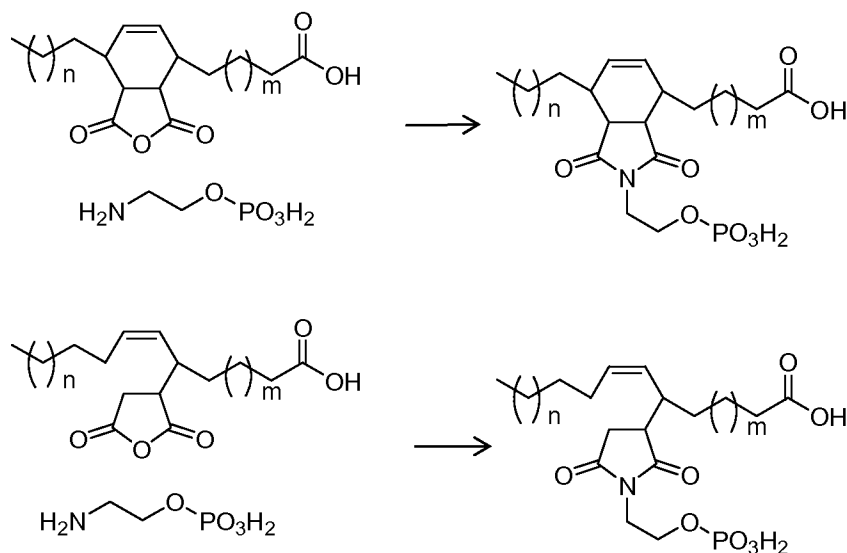
wherein R will preferably be a linear or branched hydrocarbon constituent group having from about 8 to about 24 carbon atoms.

[0015] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



wherein TOFA is tall oil fatty acid.

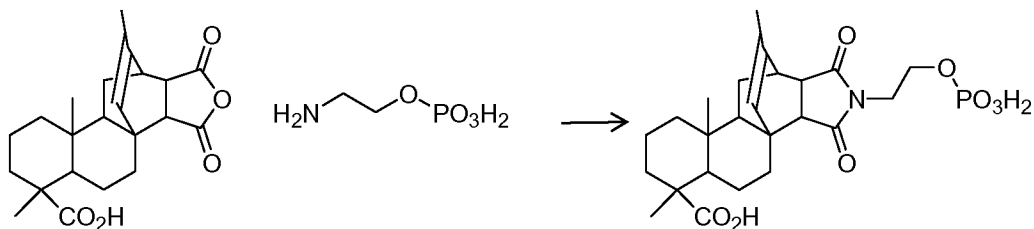
[0016] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



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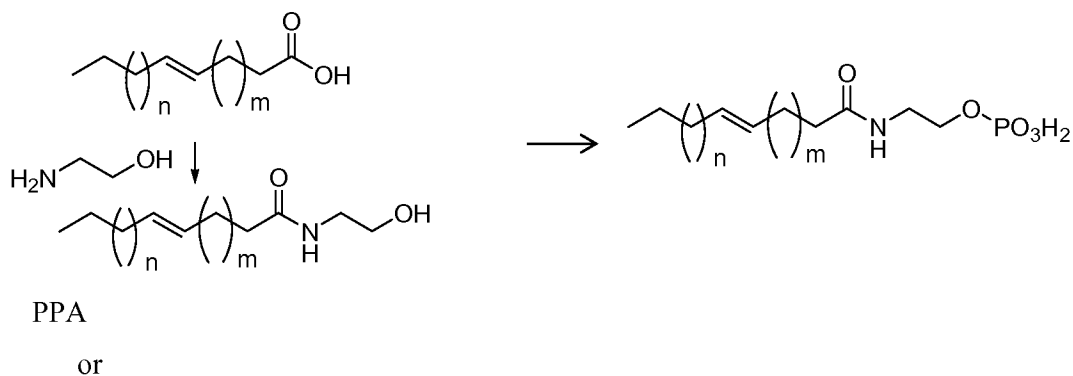
wherein $n + m$ is a value of from 2 to 12.

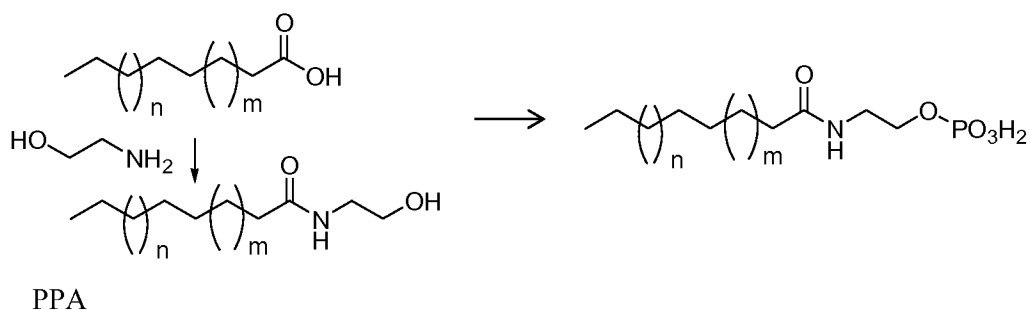
[0017] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



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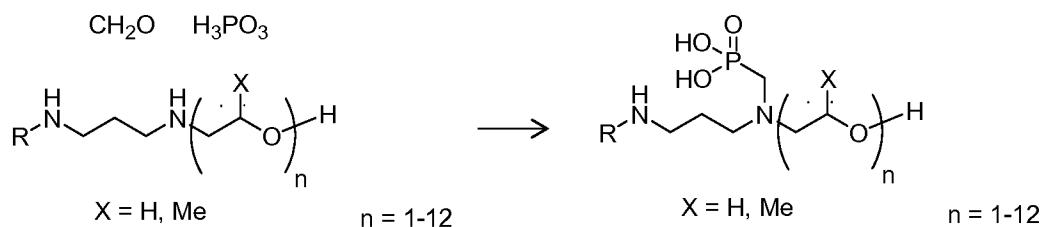
[0018] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



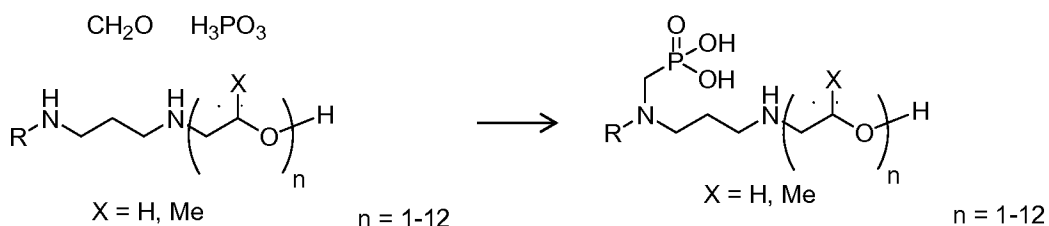


wherein $n + m$ is a value of from 1 to 12.

[0019] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



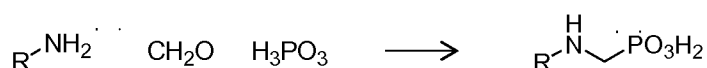
or



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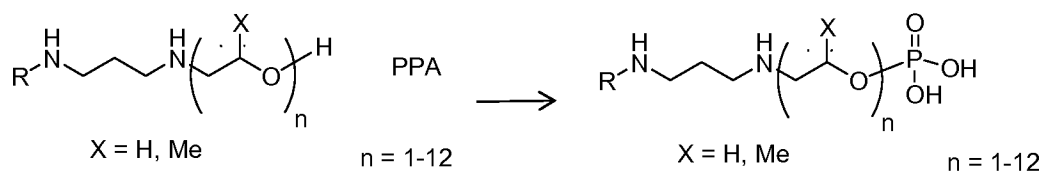
wherein: R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms; X is hydrogen or methyl group; and n is a value of from 1 to 12.

[0020] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



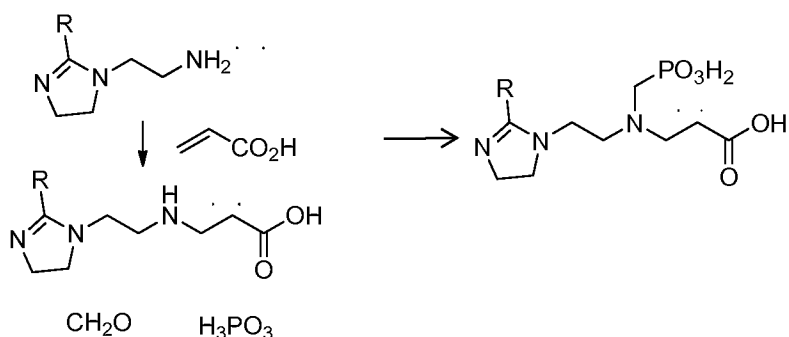
10 wherein: R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

[0021] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



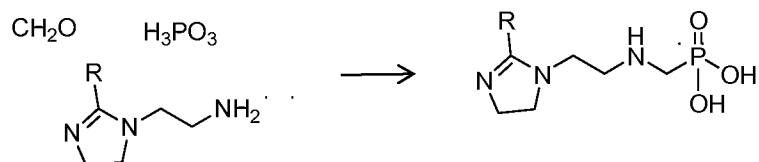
wherein: R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms and n is a value of from 1 to 12.

[0022] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



- 5 wherein: R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

[0023] A further example of a preferred traceable surfactant can be prepared in accordance with the following reaction formula:



- 10 wherein: R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

- [0024] The inventive flooding composition and method can be adapted for use in any type of reservoir flooding operation. Any one or a combination of the traceable surfactants identified above will preferably be present in the flooding composition in an amount in the range of from about 0.05% to about 2% by weight, based on the total weight of the flooding composition. The traceable surfactants will typically be in liquid or powder form and can be combined with a solvent (e.g., C₄ alcohol) when added to the flooding composition if necessary. The solvent will typically be present in an amount of from 0% to about 3% by weight based upon the total weight of the flooding composition and will also operate in the formation to lower the viscosity of the micro-emulsion which forms between the surfactant and the oil in the reservoir.
- 15
- 20

[0025] An example of one type of flooding operation which can be performed using the inventive method and flooding composition is a surfactant/polymer (SP) flood for chemical enhanced oil recovery wherein, in addition to including one or more traceable surfactants as described above, the inventive flooding composition will further
5 comprise (a) an aqueous brine solution which is tailored to the salinity of the reservoir and (b) one or more polymers of the type commonly used in the art in flooding operations to provide mobility control so that the flood front will move uniformly through the reservoir, preferably preventing viscous fingering. For this type of enhanced oil recovery procedure, the overall surfactant content of the flooding composition will preferably be in
10 the range of from about 0.5% to about 1% by weight and the polymer content of the flooding composition will preferably be in the range of from about 1000 to about 3000 ppm by weight. The traceable surfactant will be present in a concentration sufficiently high so that it can be detected in the producer wells.

[0026] As another example, the inventive method and flooding composition can
15 also be used in alkaline/surfactant/polymer (ASP) flood type procedures wherein the oil in the reservoir has a high naphthenic acid content. The alkali in the flooding composition (e.g., sodium carbonate) reacts with the naturally occurring fatty acids within the subterranean oil to produce fatty acid surfactant salts in situ, thereby decreasing the interfacial tension. The production of these surfactant salts in situ reduces the amount of
20 synthetic surfactant added to the flooding composition. Consequently, in an operation of this type, the overall amount of synthetic surfactant added to the flooding composition will preferably be in the range of from about 0.05% to about 0.2% by weight. The traceable surfactant will be present in a concentration sufficiently high so that it can be detected in the producer wells.

25 [0027] In performing the second step of the inventive method of enhanced oil recovery wherein the fluid produced from the subterranean reservoir is analyzed to determine if the traceable surfactant is present in the fluid, the phosphate, phosphonate, and/or phosphinate moieties present in the surfactant structure allow the use of simple, yet accurate, analytical techniques which can be implemented in the field.

30 [0028] As will be understood by those in the art, one such technique is a digestion procedure (e.g., metaphosphate analysis) wherein (a) the sample is first analyzed for orthophosphate, (b) total phosphate analysis is conducted on the sample by digestion with H_2SO_4 and heating for several hours to cleave the carbon phosphorus bonds, and (c) an orthophosphate analysis is subsequently conducted on the digested sample giving the total

phosphate. Metaphosphate (organic phosphorous) is the total phosphate minus the orthophosphate.

[0029] As another alternative, the sample can be analyzed for the presence of the phosphorus moieties by titration using a Palintest organophosphate pocket kit.

5 [0030] Using these analytical techniques, the operator is not only able to determine the presence of the traceable surfactant in the fluid produced from the reservoir, but can also quantify the concentration of the surfactant in the produced fluid over time.

[0031] Consequently, as noted above, the use of the inventive method and
10 flooding composition allow the user to: (1) detect the presence of the traceable surfactant in the flooding front; (2) determine when the surfactant front of the flooding composition has arrived at the producer well; (3) better analyze and understand the geology of the reservoir during trials, drill injection, etc.; (4) detect and quantify the adsorption of the flooding surfactant on the formation rock; (5) understand other phenomena occurring in
15 the reservoir during enhanced oil recovery; and (6) optimize final commercial flooding operations and other enhanced oil recovery procedures performed in the reservoir.

[0032] In addition, the inventive method and flooding composition can also provide further important information regarding the structure and geology of the reservoir. For example, given that, in most cases, an injected flood front should advance
20 through a reservoir at a rate of approximately a few feet per day, if the surfactant arrives sooner than expected, then it is likely that a high permeability streak is present in the reservoir between the injection and production wells so that the flood is by-passing much of the oil remaining in the formation. On the other hand, if the surfactant takes too long to appear, then there may be too much adsorption of the surfactant on the formation rock,
25 or the geology of the formation between the injection and production wells may be significantly different than expected.

[0033] Further, it will also be understood that the inventive method can optionally employ a plurality of traceable surfactants of the type described above which can be added to different injector wells. In this case the fronts from different injectors can be
30 detected independently at a given producer well.

[0034] The following Examples are intended to illustrate, but in no way limit, the claim invention.

EXAMPLE 1

Preparation of tallow diamine ethoxylate (m = 8) methylene phosphate salt.

[0035] Into a round bottomed flask equipped with reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 62.51 g of 8-mol-ethoxylate tallow diamine and 4.36 g of paraformaldehyde. While introducing nitrogen into the flask, the temperature was slowly increased to 80°C. A solution of 9.65 g 30% HCl aq, 8.68 g phosphorous acid in 74.83 g water was added dropwise. The reaction mixture was stirred for three hours at 90°C. After the resulting mixture was cooled to 80°C isopropyl alcohol, IPA was added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out and neutralized.

EXAMPLE 2

Preparation of imidazoline ethoxylate (m = 8) phosphite salt.

[0036] Into a round bottomed flask equipped with reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 75.48 g of 8-mol-ethoxylate imidazoline and 9.15 g of polyphosphoric acid (Aldrich). While introducing nitrogen into the flask, the mixture was stirred and mixed well for one hour at room temperature. The temperature was slowly increased to 90°C. The reaction mixture was stirred for five hours at this temperature. After the resulting mixture was cooled to 80°C, water and IPA were added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out and neutralized.

EXAMPLE 3

Preparation of Adogen 170S methylene phosphate salt.

[0037] Into a round bottomed flask equipped with reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 48.50 g of Adogen 170S (available from Evonik) and 8.36 g of paraformaldehyde. While introducing nitrogen into the flask, the temperature was slowly increased to 80°C. A solution of 19.32 g 30% HCl aq, 15.10 g phosphorous acid in 75.31 g water was added dropwise. The reaction mixture was stirred for three hours at 90°C. After the resulting mixture was cooled to 80°C, IPA was added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out.

EXAMPLE 4

Preparation of fatty acid imidazoline acrylic acid methylene phosphate salt.

[0038] Into a round bottomed flask equipped with reflux condenser, nitrogen inlet,

temperature probe, and stirrer, there were charged 60.16 g of fatty acid imidazoline (Polyfac T-903), 11.56 g of acrylic acid and 88.42 g of acetonitrile. The reaction mixture was stirred for six hours at temperature 85°C under the nitrogen. After the reaction, the acetonitrile was removed. The reaction mixture was cool to room temperature and 6.30 g of pararformaldehyde was added in. While introducing nitrogen into the flask, the temperature was slowly increased to 80°C. A solution of 19.36 g 30% HCl aq, 12.24 g phosphorous acid in 25.63 g water was added dropwise. The reaction mixture was stirred for three hours at 90°C. After the resulting mixture was cooled to 80°C, IPA was added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out and neutralized.

EXAMPLE 5

Preparation of phosphoric acid tagged tall oil fatty acid (TOFA).

[0039] 41.64 g of ethanol amine was heated to 50°C under nitrogen. 10.16 g of polyphosphoric acid (Aldrich) was added in. After addition, the reaction mixture was slowly heated to 100 °C and was allowed to proceed for four hours at 100°C - 120°C. After the resulting mixture was cooled to 80°C, IPA was added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out.

EXAMPLE 6

Preparation of tallow diamine ethoxylate (8) phosphate.

[0040] Into a round bottomed flask equipped with reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 61.51 g of 8-mol-ethoxylate tallow diamine and 8.92 g of polyphosphoric acid (Aldrich). While introducing nitrogen into the flask, the mixture was stirred and mixed well for one hour at room temperature. The temperature was increased to 45°C and the reaction mixture was stirred for two hours at 45°C. Then the temperature was slowly increased to 85°C. The reaction mixture was stirred for four hours at this temperature. After the resulting mixture was cooled to 80°C, water and IPA were added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out.

EXAMPLE 7

Preparation of tall oil fatty acid polyamine condensate methylene phosphonic acid.

[0041] Into a round bottomed flask equipped with reflux condenser, nitrogen

inlet, temperature probe, and stirrer, there were charged 60.57 g of tall oil fatty acid polyamine condensate; while introducing nitrogen into the flask, the temperature was slowly increased to 70°C. 4.77 g of paraformaldehyde was added in and the reaction mixture was stirred for 0.5 hour. A pre-mixed solution of 8.35 g 30% HCl aq, 8.11 g phosphorous acid in 44.99 g water was added dropwise. The reaction mixture was stirred for three hours at 90°C. After the resulting mixture was cooled to 80°C, IPA was added. The reaction mixture was stirred for another hour at this temperature before being cooled to room temperature. The reaction mixture was poured out.

10

EXAMPLE 8

Winsor III screening test procedure.

[0042] Aqueous solutions of NaCl in concentrations of 0.1-15 wt. percent were prepared with deionized water. Various surfactant solutions of appropriate HLB numbers were prepared from concentrations of 0.5-2.0 wt. percent in 50 mL plastic bottles. Into clean and dry 10 mL scintillation vials was injected Sigma Aldrich HPLC grade 1.5 mL of dodecane. As is common in lab simulation procedures, the dodecan was used to simulate crude oil. Using a separate syringe, 1.5 mL of surfactant solutions were injected into the scintillation vials and the vials were capped. The vials were stirred vigorously using a vortex mixer for 10 seconds. The vials were allowed to sit undisturbed at room temperature and the presence or absence of a Windsor III phase was observed after 16 hours of equilibration.

[0043] All of the surfactant solutions produced a Windsor III microemulsion phase, thereby displaying minimum surface tension performance desirable for displacement in enhanced oil recovery procedures. Table 1 lists the conditions at which the Winsor III behavior occurred.

Table 1. Conditions for forming Winsor Type III Systems

	<u>Primary Surfactant</u>	<u>Primary Surfactant Concentration (wt. %)</u>	<u>Cosurfactant</u>	<u>Cosurfactant Concentration</u>	<u>Total surfactant concentration</u>	<u>Brine concentration</u>
1	Tallow diamine ethoxylate (8) methylene phosphate salt	0.33%	TOFA	0.67%	1%	8%
2	Imidazoline ethoxylate (8) phosphate salt	0.33%	TOFA	0.67%	1%	8%
3	Adogen 170S methylene phosphate salt	0.25%	Phosphate-tagged TOFA	0.25%	0.50%	0%
4	Fatty acid imidazoline acrylic acid methylene phosphate salt	100%	none	0%	1.00%	12.5-15.0%

EXAMPLE 9

ICP detection of tagged surfactants.

[0044] Phosphorus ICP (Inductively Coupled Plasma) standards were made gravimetrically using a stock 1000 ppm phosphorous standard and diluting with deionized water with less than 1% error. The 1000 ppm calibration standard was the stock phosphorus solution. Seven calibration standards (25, 50, 100, 300, 600, 800, and 1000 ppm) were run on an Agilent 715 radial ICP-OES at 214.914 nm wavelength in triplicate. The average value was reported as the standard concentration within the instrument acceptable 20% error, yielding a calibration correlation coefficient of 0.999572. Following the calibration, two check standards: 25 ppm and 100 ppm were run with results of 20.0106 ppm and 100.744 ppm respectively; both within instrument acceptable 20% error.

[0045] Samples were prepared by diluting with deionized water to approximately the middle of the calibration range. Each sample was run in triplicate with the average concentration being reported in ppm. As Table 2 shows, the surfactant concentration could be calculated from the tag with minimal error.

Table 2. Detectability of tagged surfactants

<u>Sample</u>	<u>Actual concentration (ppm)</u>	<u>Measured concentration (ppm)</u>	<u>Error (%)</u>
0.25% Adogen 170S methylene phosphate salt 0.25 wt% Phosphate-Tagged TOFA	307.6	306.8	0.3
Tallow diamine ethoxylate (8) methylene phosphate salt	22.6	22.6	0.0
Fatty acid imidazoline acrylic acid methylene phosphate salt	386.2	399.4	-3.4
Imidazoline ethoxylate (8) phosphate salt	125.6	125.6	0.0

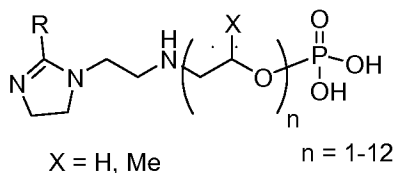
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[0046] Thus, the present invention is well adapted to carry out the objectives and attain the ends and advantages mentioned above as well as those inherent therein. While presently preferred embodiments have been described for purposes of this disclosure, numerous changes and modifications will be apparent to those of ordinary skill in the art. Such changes and modifications are encompassed within this invention as defined by the claims.

CLAIMS

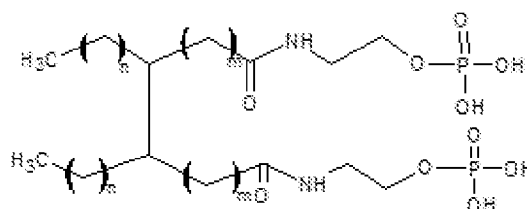
What is claimed is:

1. A method of enhanced oil recovery from a subterranean reservoir comprising the steps of:
 - (a) delivering a flooding composition into said subterranean reservoir, said flooding composition including a traceable surfactant having at least one traceable phosphorus moiety and
 - (b) analyzing a fluid produced from said subterranean reservoir to determine if said traceable surfactant is present in said fluid.
2. The method of claim 1 wherein said traceable surfactant includes a phosphate moiety, a phosphonate moiety, a phosphinate moiety, or a combination thereof.
3. The method of claim 2 wherein said traceable surfactant is present in said flooding composition in an amount of from about 0.05% to about 2% by weight.
4. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



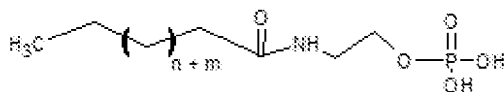
wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms, X is hydrogen or a methyl group, and n is a value of from 1 to 12.

5. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



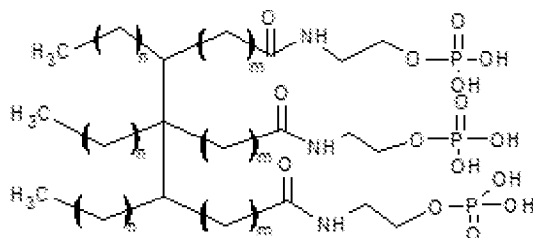
wherein $n + m$ is a value of from 10 to 22.

6. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



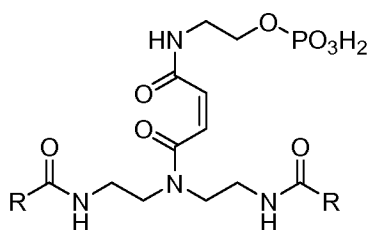
wherein $n + m$ is a value of from 10 to 22.

7. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



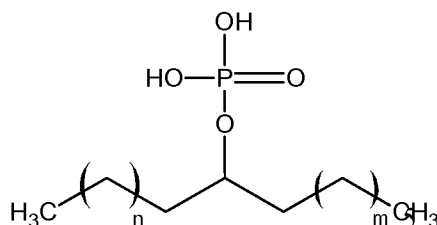
wherein $n + m$ is a value of from 10 to 22,

8. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



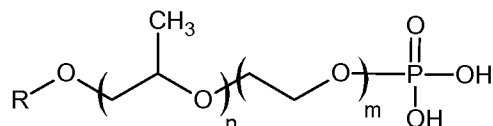
wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

9. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



wherein $n + m$ is a value of from about 11 to 19.

- 10.** The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



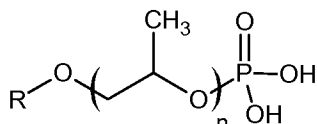
wherein R is a linear or branched hydrocarbon constituent group having from 8 to 30 carbon atoms, n is a value of from 0 to 100, and m is a value of from 0 to 100.

- 11.** The method of claim 10 wherein:

n is a value of from 2 to 15 and

m is a value of from 2 to 15.

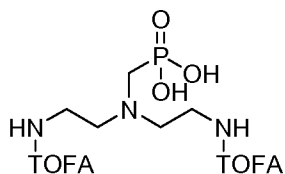
- 12.** The method of claim 1 wherein a said traceable surfactant comprises one or more compounds having the formula:



wherein R is a linear or branched hydrocarbon constituent group having from 8 to 30 carbon atoms and n is value of from 0 to 100.

- 13.** The method of claim 12 wherein n is a value of from 2 to 15.

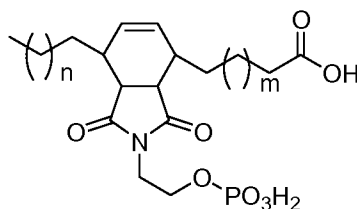
14. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



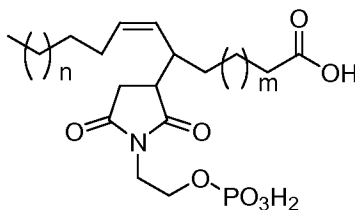
wherein TOFA is tall oil fatty acid.

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15. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



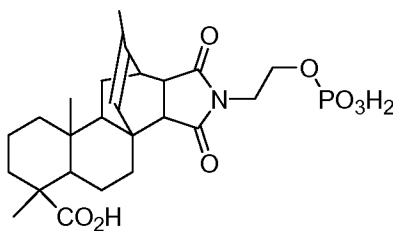
or



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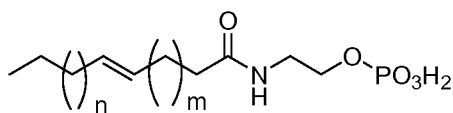
wherein $n + m$ is a value of from 2 to 12.

16. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:

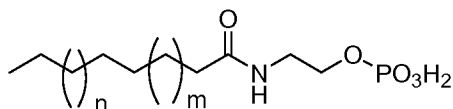


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17. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



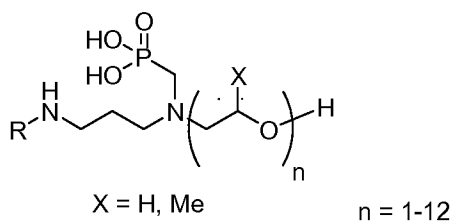
or



wherein $n + m$ is a value of from 1 to 12.

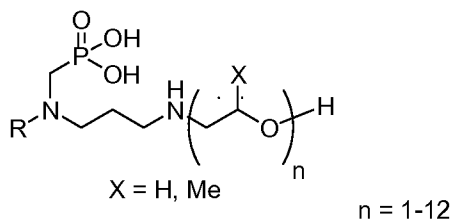
5

18. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



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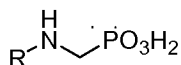
or



wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms, X is hydrogen or a methyl group, and n is a value of from 1 to 12.

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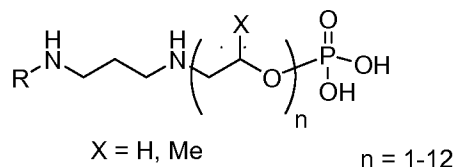
19. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



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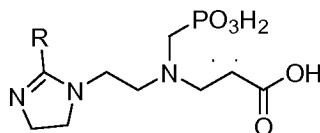
wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

20. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having a formula:



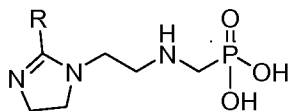
wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms, X is hydrogen or a methyl group, and n is a value of from 1 to 12.

21. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having formula:



wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

22. The method of claim 1 wherein said traceable surfactant comprises one or more compounds having formula:



wherein R is a linear or branched hydrocarbon constituent group having from 8 to 24 carbon atoms.

23. The method of claim 1 wherein said fluid is analyzed in step (b) by digestion or titration.

24. The method of claim 23 wherein said step (b) of analyzing said fluid produced from said subterranean reservoir also provides a concentration of said traceable surfactant in said fluid.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/025381

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/584
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)
C09K

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)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 094 798 A (TATE JACK F ET AL) 13 June 1978 (1978-06-13) column 7, line 41 - column 8, line 39 the whole document -----	1-23
X	WO 2012/098186 A1 (RHODIA OPERATIONS [FR]; JONES CHRIS [GB]; LABARRE DOMINIQUE [FR]; ROUA) 26 July 2012 (2012-07-26) page 13, line penultimate; claims 1, 2 the whole document -----	1-24
X	US 2012/292025 A1 (STOLL WERNER MARTIN [OM]) 22 November 2012 (2012-11-22) paragraph [0134]; claims 1-3 the whole document ----- -/--	1-24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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

12 May 2014

Date of mailing of the international search report

19/05/2014

Name and mailing address of the ISA/

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Straub, Thomas

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/025381

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 489 714 A (TRACESA LTD [GB]) 10 October 2012 (2012-10-10) claims 27,49-56,60-65 the whole document -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/025381

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			WO 2012136734 A1	11-10-2012
