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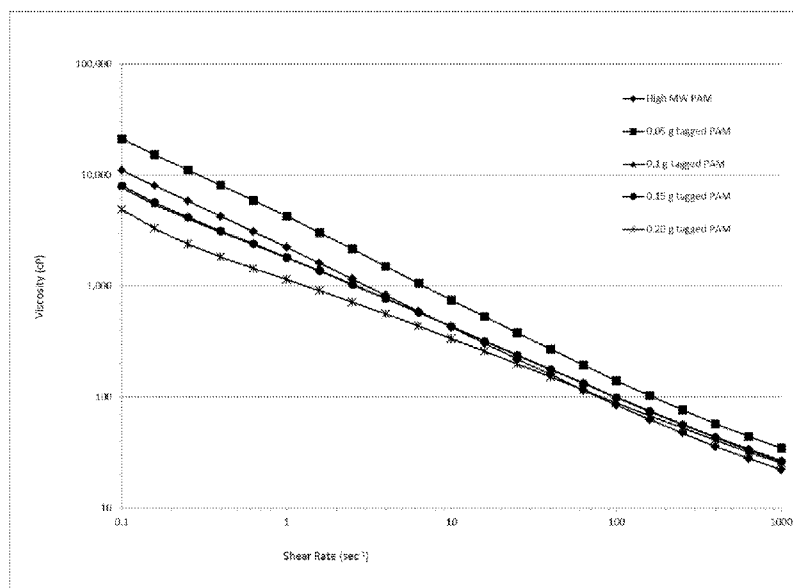
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(54) Title: TRACEABLE POLYMERIC VISCOSIFIER COMPOSITIONS AND METHODS OF USING

FIG. 2



(57) Abstract: A traceable polymeric viscosifier which includes traceable phosphinate and/or phosphonate moieties and a viscosifying moiety. The viscosifying moiety may include amide functionality as well as carboxylate functionality and/or sulfonate functionality. The traceable polymeric viscosifier is suitable for enhanced oil recovery (EOR) in oilfield operations. A method of recovering petroleum from subterranean a petroleum-bearing deposit using an aqueous solution of the traceable polymeric viscosifier is also provided. The solution is preferably injected into a deposit area through at least one injection well to cause petroleum to flow from the deposit area for collection through at least one production well. The phosphinate and/or phosphonate moieties on the traceable polymeric viscosifier allow detection of the advancement of the water injection through the oil reservoir during the EOR application.

TRACEABLE POLYMERIC VISCOSIFIER COMPOSITIONS AND METHODS OF USING

FIELD OF THE DISCLOSURE

5 **[0001]** Embodiments of the present disclosure relate to traceable polymeric viscosifier compositions and to methods of using such compositions in oilfield applications.

BACKGROUND OF THE DISCLOSURE

10 **[0002]** Petroleum recovery in oilfield operations may be divided into a primary recovery, a secondary recovery, and a tertiary recovery processes. A primary recovery process refers to petroleum recovery operations when petroleum spontaneously flows from a wellbore or by using conventional pumps. After a primary recovery process, very large amounts of petroleum in a given reservoir remain unrecovered. A secondary
15 recovery process refers to petroleum recovery operations when spontaneous production of petroleum from the wellbore can no longer take place, and re-injection of formation brine or natural gas from the formation is required to maintain the reservoir pressure. Secondary recovery begins when primary recovery is no longer feasible and continues for as long as there is any petroleum left in the reservoir which can be economically or
20 feasibly removed. The tertiary recovery process begins when the petroleum reservoir is substantially "flooded out," and the oil cuts (i.e., volume fraction of oil in the produced crude) fall to levels that make secondary recovery economically unfeasible.

[0003] To further improve oil recovery, a variety of tertiary recovery techniques, typically referred to as Enhanced Oil Recovery (EOR), have been employed including
25 miscible techniques such as gas flooding; thermal methods such as heating or steam injection; and chemical methods such as Polymer (P), Surfactant/Polymer (SP) or Alkaline/Surfactant/Polymer (ASP) flooding. Solvents and other chemicals, such as biocides, wax inhibitors, asphaltene inhibitors, etc., are sometimes injected in SP and ASP floods to assure that no undesired precipitates are formed from the oil that can
30 impede flow in the porous formation. These solvents and other chemicals may also reduce the viscosity of the micro-emulsion formed between the oil, water and surfactant. This micro-emulsion has droplets which are small enough to flow through the pore-throats of the formation porous medium. Furthermore, chemical EOR formulations sometimes contain biocides to mitigate the risk of bacterial buildup and oxygen

scavengers to reduce the levels of oxygen in the water, which can degrade the polymer thereby decreasing its molecular weight.

[0004] EOR processes using water flooding techniques have been widely used to recover the vast quantity of unrecovered petroleum (oil) left in the reservoir when oil can no longer be produced from the reservoir economically using conventional production techniques. EOR flooding techniques comprise injecting a water-based solution into the petroleum bearing formation through at least one injection well, thereby causing oil to flow from that area to at least one production well. Water is typically pumped into one or more injection wells, under a high enough pressure to force the oil to flow through the petroleum-bearing formation, but not high enough to fracture the formation. The oil remaining in the formations is forced out by the oncoming water solution and removed through the production wells. Oftentimes, patterns of injection and production wells are established over an oil field in a manner that will optimize the EOR recovery operation by taking into account the geological aspects of that particular field.

[0005] Ideally, water should displace 100% of the petroleum in the oil field. In practice, water may by-pass many parts of the reservoir rock as the water front passes through a reservoir. This may be due to, for example, an inherent incompatibility of petroleum and water, variations in reservoir rock including permeability variation, faults and shale barriers. The ability of water or any other fluid to displace petroleum depends on the mobility of that fluid in relation to that of the oil. Every fluid has a specific mobility in an oil reservoir, which can be defined as the ease with which that fluid flows through a porous medium (permeability) divided by the viscosity of that fluid. If a fluid flows much more easily than petroleum through a reservoir, the fluid will readily bypass the oil deposits within the reservoir rather than displacing oil toward production wells. This is called viscous fingering by those skilled in the art. Thus, invading water-based solutions with low mobility are greatly preferred for chemical EOR applications. The recovery efficiency of chemical EOR techniques is greatly enhanced by increasing the ratio of the oil mobility over the injection water-based solution mobility. This may be accomplished by increasing viscosity of injection water-based solution and/or decreasing the viscosity of petroleum through addition of suitable chemical agents or by thermal means. Commonly, a thickening agent is added to the injection water to enhance the viscosity of the injection water-based solution.

[0006] Water-soluble polymers with molecular weight of above 1,000,000 may be

added to the injection water used in EOR applications to increase the viscosity of injection water, and thereby decreasing the mobility of injection water in relation to that of the petroleum. Polyacrylamides are widely used as water-soluble polymeric viscosifiers. For example, U.S. Patent No. 4,592,850, issued on June 3, 1986 to

5 Goodyear Tire & Rubber Company discloses high molecular weight N, N-dimethylacrylamide copolymers and terpolymers suitable as injection water viscosifiers for EOR process of oilfield operations. U.S. Patent No. 4,702,319, issued on October 27, 1987 to Exxon Research and Engineering Company, discloses polymeric viscosifiers for enhanced oil recovery comprising a hydrophobically associating terpolymer of

10 (meth)acrylamide, a salt of an ethylenically unsaturated sulfonic acid, and an N-alkyl(meth)acrylamide.

[0007] Performance of many polymeric viscosifiers is adversely affected by levels of dissolved ions typically found in the subterranean formations, placing limitations on their use and/or effectiveness in EOR applications. For example, the viscosity of

15 polyacrylamide viscosifier decreases with water salinity and divalent ion concentration. However, in practice the salinity of the injection water must be compatible with that of the formation water in order to prevent precipitates from the oil and to allow the surfactant to work under optimal conditions. A fresh water source (i.e., water having total dissolved solids of less than 10,000 ppm) is optimal for the effective use of

20 polyacrylamides as viscosifiers in EOR applications. Higher total dissolved solids will require higher concentrations of polymer to achieve optimal mobility ratios.

SUMMARY OF THE DISCLOSURE

[0008] In some embodiments, a traceable polymeric viscosifier includes a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety comprising

25 amide functionality. In one embodiment, a traceable polymeric viscosifier includes a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety comprising amide functionality and at least one of carboxylate functionality and sulfonate functionality.

[0009] In some embodiments, an aqueous formulation for chemical EOR

30 applications comprises a traceable polymeric viscosifier that includes a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety comprising amide functionality. In one embodiment, an aqueous formulation for chemical EOR applications comprises a traceable polymeric viscosifier that includes a viscosifying

moiety and a traceable phosphinate and/or phosphonate moieties, the viscosifying moiety comprising amide functionality and at least one of carboxylate functionality and sulfonate functionality.

[0010] Certain embodiments relate to a method of recovering petroleum from
5 subterranean petroleum-bearing formation includes injecting an aqueous solution into the formation through at least one injection well to cause the petroleum to flow from the injection well area to at least one production well, wherein the aqueous solution comprises a traceable polymeric viscosifier including a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety comprising amide functionality. In one
10 embodiment, a method of recovering petroleum from subterranean petroleum-bearing formation includes injecting an aqueous solution into the formation through at least one injection well to cause the petroleum to flow from the injection well area to at least one production well, wherein the aqueous solution comprises a traceable polymeric viscosifier including a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety
15 comprising amide functionality and at least one of carboxylate functionality and sulfonate functionality.

[0011] Further embodiments relate to a method of detecting an advancement of water injection through an oil reservoir during an EOR application. The method comprises applying an injection water comprising a traceable polymeric viscosifier to the
20 oil reservoir under pressure to force the oil to a production well, the traceable polymeric viscosifier including a viscosifying moiety and a traceable phosphinate and/or phosphonate moieties; taking a sample of reservoir fluid; and measuring a concentration of the traceable phosphinate and/or phosphonate moieties in the reservoir fluid sample to determine the advancement of the water injection front through the oil reservoir.

25 BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 shows a plot of the concentration of traceable phosphinate moiety as determined by Palintest Organophosphonate titration method as a function of the concentration of traceable polymeric viscosifier.

[0013] Fig. 2 shows the viscosity as a function of Shear Rate curves for High
30 Molecular Weight PAM and chemically modified High Molecular Weight PAM with different weight percents of tag.

DESCRIPTION OF THE DISCLOSURE

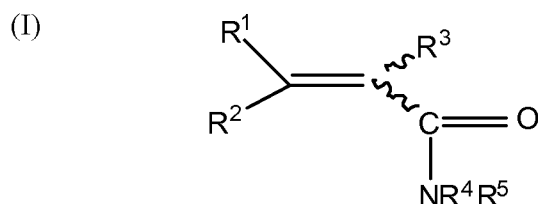
[0014] The present disclosure now will be described more fully hereinafter, but not all embodiments of the disclosure are shown. While the disclosure has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the disclosure without departing from the essential scope thereof.

[0015] In a particular embodiment, a traceable polymeric viscosifier may comprise a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety comprising amide functionality.

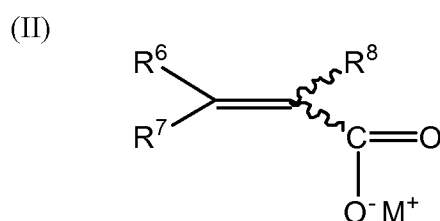
[0016] In one embodiment, the traceable polymeric viscosifier may be prepared from a mixture comprising: a phosphinate compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, and combinations thereof; and an amide monomer capable of being at least partially hydrolyzed. Various amide monomers may be used including, but not limited to, vinylacrylamide; N-substituted acrylamides such as N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-ethylmethacrylamide; N,N-substituted acrylamide such as N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N,N-diethylacrylamide, N,N-diethylmethacrylamide, and the like. The resulting polymer may then be partially hydrolyzed. A variety of alkaline salts may be used for hydrolysis including, but not limited to, sodium carbonate, sodium hydroxide, sodium sulfate, or combinations thereof. The degree of hydrolysis may be from about 0% to 60%.

[0017] In one embodiment, the traceable polymeric viscosifier may comprise a traceable phosphinate and/or phosphonate moieties and a viscosifying moiety comprising amide functionality and at least one of carboxylate functionality and sulfonate functionality.

[0018] In one embodiment, the traceable polymeric viscosifier may be prepared from a mixture comprising: a phosphinate compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, and combinations thereof; an amide monomer represented by structure (I),



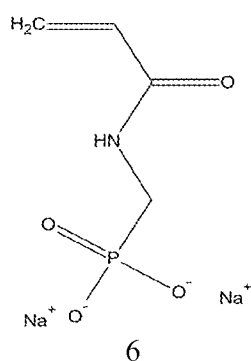
- 5 R^1 , R^2 and R^3 each being independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group; R^4 and R^5 each being independently hydrogen, an alkyl group containing up to 7 carbon atoms, an alkoxy group containing up to 7 carbon atoms, or a phosphonate group; and a carboxylate monomer represented by structure (II),



- 10 R^6 , R^7 and R^8 are independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group; and M is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ where R_1 , R_2 , R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbons.

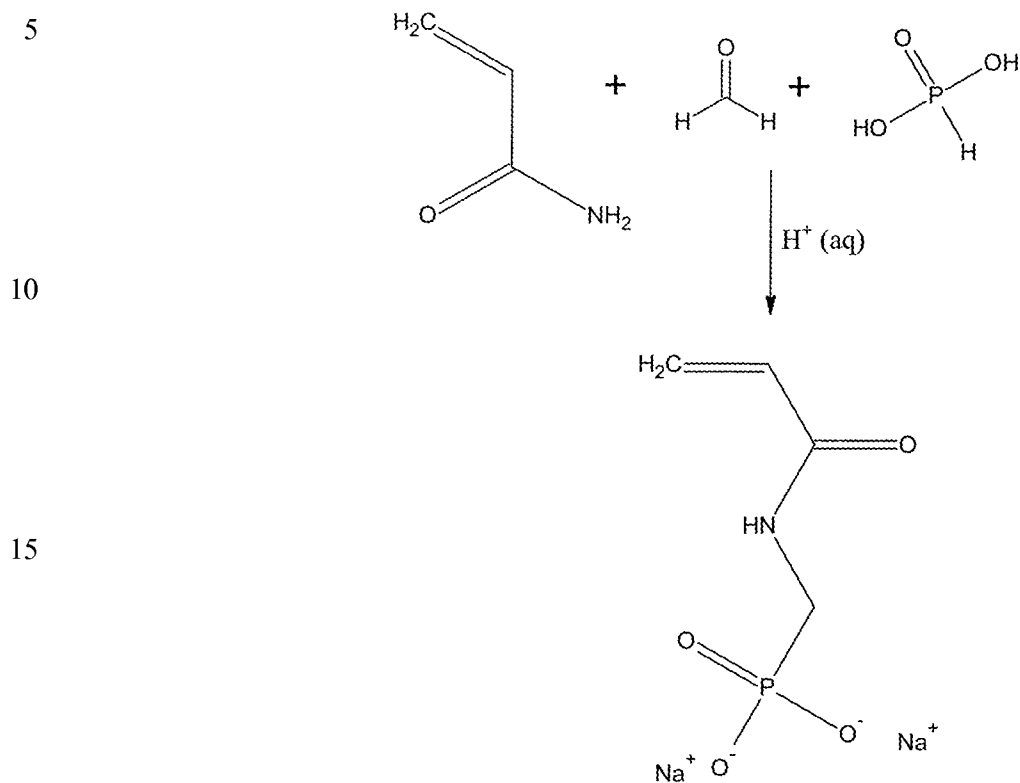
[0019] Various amide monomers represented by structure (I) may be used including, but not limited to, vinylacrylamide; N-substituted acrylamides such as N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-ethylmethacrylamide; N,N-substituted acrylamide such as N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N,N-diethylacrylamide, N,N-diethylmethacrylamide, and the like. Additionally, the amide monomer may contain a phosphonate moiety and have structure (A):

(A)



[0020] The amide monomer of structure (A) may be prepared as shown in formula (B):

(B)

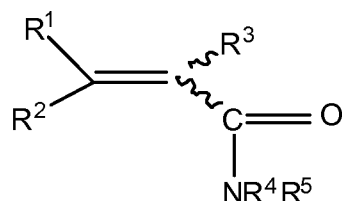


[0021] Carboxylate monomers represented by structure (II) may include, but are not limited to, monocarboxylic acid monomers such as acrylic acid, oligomeric acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid and the water-soluble salts thereof; unsaturated dicarboxylic acid monomers such as unsaturated dicarboxylic acid monomers containing 4–10 carbon atoms per molecule and anhydrides of the cis-dicarboxylic acids; or unsaturated monomer containing more than two carboxylic acid groups such as polyacid. Non-limiting examples of unsaturated dicarboxylic acid monomers may be maleic acid; maleic anhydride; fumaric acid; itaconic acid; citraconic acid; mesaconic acid; cyclohexenedicarboxylic acid; cis-1,2,3,6-tetrahydrophthalic anhydride; 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride; and water-soluble salts thereof.

[0022] In one embodiment, the traceable polymeric viscosifier may be prepared from a mixture comprising: a phosphinate compound selected from the group consisting

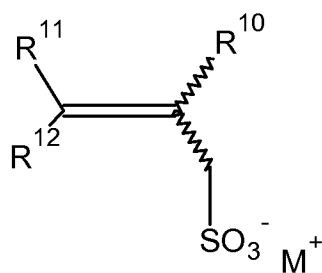
of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, and combinations thereof; an amide monomer represented by structure (I),

(I)

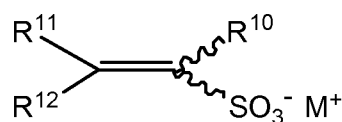


R^1 , R^2 and R^3 each being independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group; R^4 and R^5 each being independently hydrogen, an alkyl group containing up to 7 carbon atoms, an alkyl group containing up to 7 carbon atoms, an alkoxy group containing from 1 to 7 carbon atoms, or a phosphonate group; and a sulfonate monomer represented by structure (III) or (IV),

(III)



(IV)



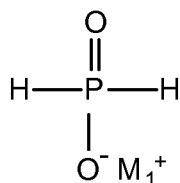
R^{10} , R^{11} and R^{12} each being independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group; M being hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ where R_1 , R_2 , R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbons.

[0023] Many sulfonate monomers represented by structure (III) or (IV) may be used including, but not limited to, salts of vinyl sulfonate, 2-sulfoethyl methacrylate, 2-acrylamido-2-methylpropane sulfonate, styrene sulfonate, or combinations thereof.

[0024] In one embodiment, the traceable polymeric viscosifier may be prepared from a mixture comprising: a phosphinate compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, and combinations thereof; an amide monomer represented by structure (I); a carboxylate monomer represented by structure (II); and a sulfonate monomer represented by structure (III) and/or (IV).

[0025] Phosphinate compounds suitable for present disclosure may be represented by structure (V):

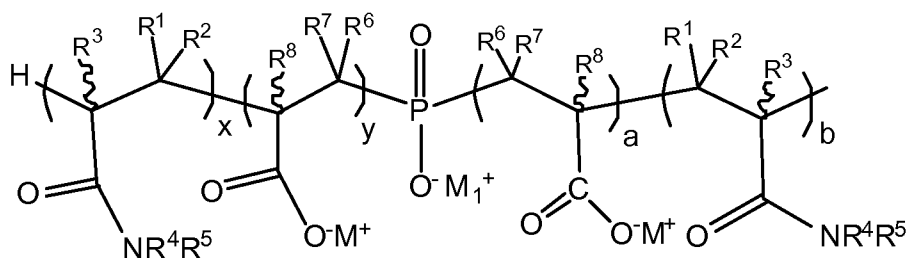
(V)



wherein M_1 is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ where R_1 , R_2 , R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbons. Various phosphinate compounds with the represented structure (V) may be used including, but not limited to, hypophosphite, inorganic phosphinate salts, organic phosphinate salt, or combinations thereof.

[0026] In one embodiment, the traceable polymeric viscosifier may comprise structure (VI):

(VI)

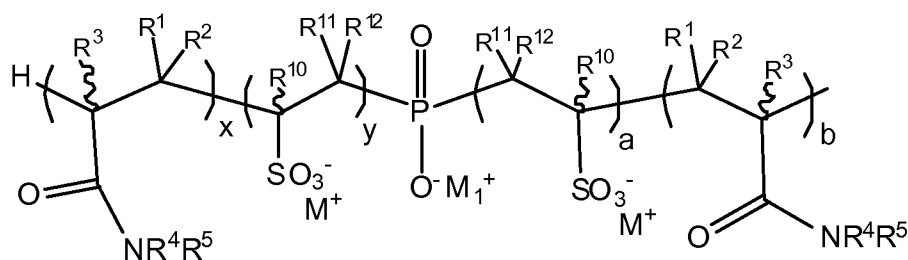


wherein

$R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 each are independently hydrogen, an alkyl group containing up to 7 carbon atoms, hydroxyl, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy group having from 1 to 7 carbons, or phosphonate group; M and M_1 are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $NR_1R_2R_3R_4$ where R_1, R_2, R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbons; x and y are independently integral numbers, a sum of x plus y being greater than 2; and a and b are independently integral numbers, a sum of a plus b being greater than 2.

[0027] In another embodiment, the traceable polymeric viscosifier may comprise structure (VII):

(VII)

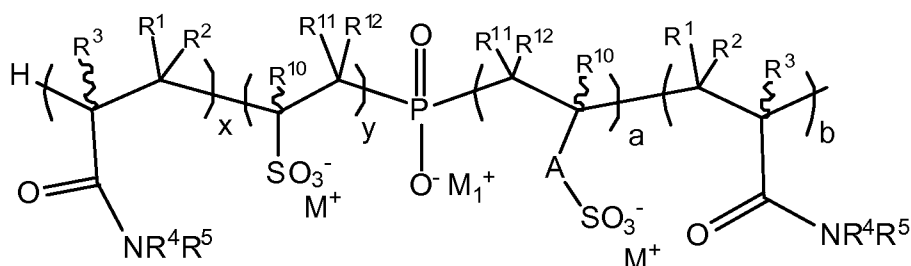


wherein

$R^1, R^2, R^3, R^4, R^5, R^{10}, R^{11}$ and R^{12} each are independently hydrogen, an alkyl group containing up to 7 carbon atoms, hydroxyl, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy group having from 1 to 7 carbons, or phosphonate group; M and M_1 each are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $NR_1R_2R_3R_4$ where R_1, R_2, R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbons; x and y are independently integral numbers, a sum of x plus y being greater than 2; and a and b are independently integral numbers, a sum of a plus b being greater than 2

[0028] In a particular embodiment, the traceable polymeric viscosifier may comprise structure (VIII):

(VIII)

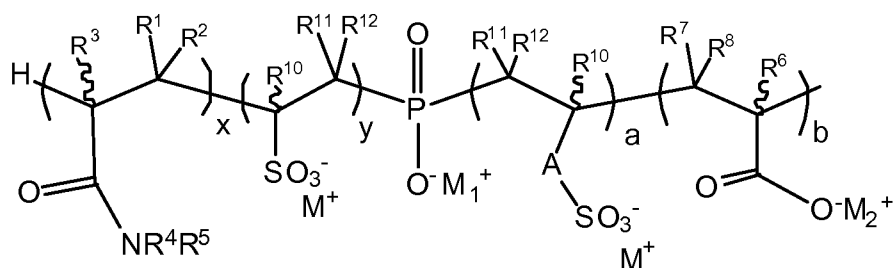


wherein

- $R^1, R^2, R^3, R^4, R^5, R^{10}, R^{11}$ and R^{12} each are independently hydrogen, an alkyl group containing up to 7 carbon atoms, hydroxy, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy group having from 1 to 7 carbons, or phosphonate group; M and M_1 each are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $NR_1R_2R_3R_4$ where R_1, R_2, R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbons; x and y are independently integral numbers, a sum of x plus y being greater than 2; and a and b are independently integral numbers, a sum of a plus b being greater than 2.

- [0029]** In another embodiment, the traceable polymeric viscosifier may comprise structure (IX):

(IX)



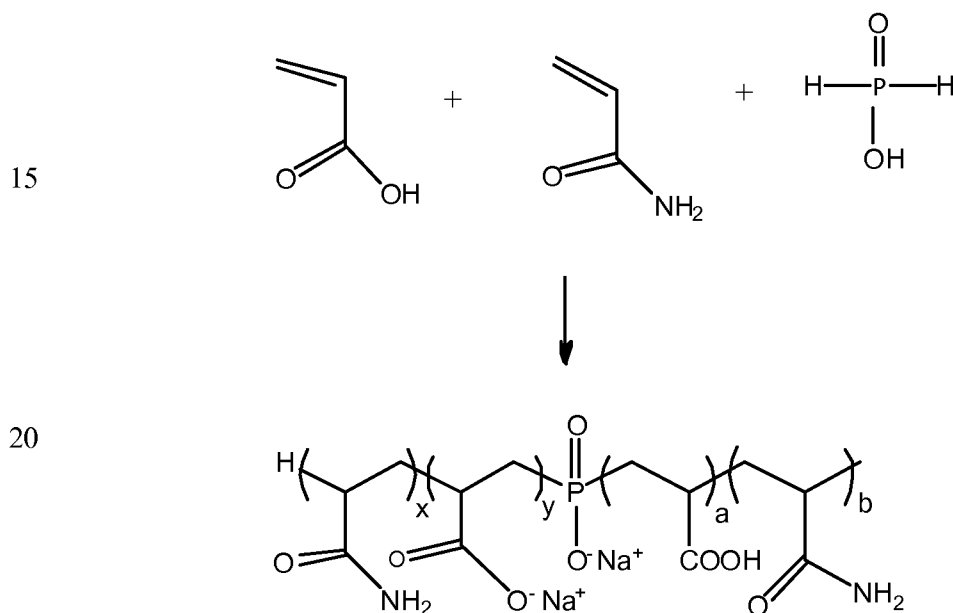
wherein

- $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^{10}, R^{11}$ and R^{12} each are independently hydrogen, an alkyl group containing up to 7 carbon atoms, hydroxyl, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy

group having from 1 to 7 carbons, or phosphonate group; M, M₁ and M₂ each are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or NR₁R₂R₃R₄ where R₁, R₂, R₃ and R₄ are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbons; x and y are independently integral numbers, a sum of x plus y being greater than 2; and a and b are independently integral numbers, a sum of a plus b being greater than 2.

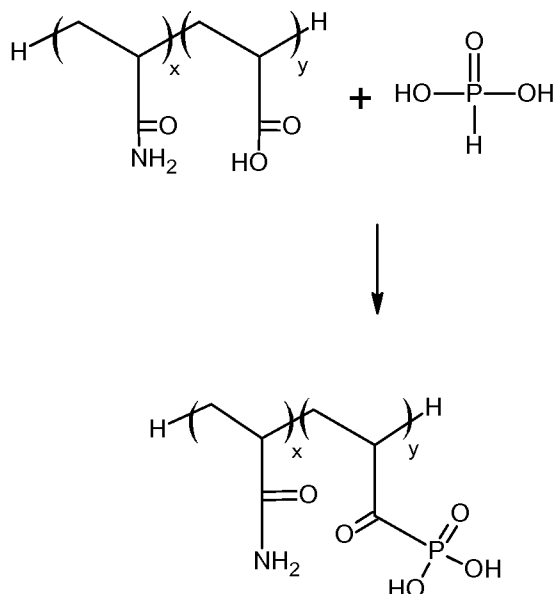
[0030] In a particular embodiment, the traceable polymeric viscifier may comprise the polymer prepared from acrylamide monomers, acrylic acid monomers, and phosphinate salt by a polymerization process, as shown in formula (X):

(X)



[0031] In another embodiment, the traceable polymeric viscifier may be a structure prepared by polymerizing acrylamide and acrylic acid together then adding phosphorous acid to tag the polymer as shown in formula (XI):

(XI)



wherein

x and y are independently integral numbers with the sum of x and y being greater than 2.

[0032] Any suitable polymerization process may be used to produce the traceable polymeric viscosifier. Those skilled in the art are familiar with various polymerization processes. The proportion of the chemicals (e.g. monomer, initiator, chain transferring agent, etc.) employed in the polymerization may be varied to a considerable extent, depending upon the particular polymeric composition and the molecular weight of the polymers desired.

[0033] The traceable polymeric viscosifier may be prepared by various free-radical polymerization processes.

[0034] The traceable polymeric viscosifier may be prepared by redox polymerization at a temperature range of about 5°C to about 50°C. Various redox initiators may be used for the polymerization including, but not limited to, persulfate (e.g., potassium persulfate and ammonium persulfate) used alone, or used in conjunction with sodium metabisulfate, sodium thiosulfate, and/or sodium dithionite and the addition of a suitable metal catalyst such as iron (Fe(II)SO₄), copper(Cu(II)SO₄) etc.

[0035] The traceable polymeric viscosifier may be prepared by free radical polymerization using a known free-radical initiator including, but not limited to, persulfate initiators such as ammonium persulfate, sodium persulfate and potassium

persulfate; azo initiators such as azoisobutyronitrile (AIBN); organic or inorganic peroxides such as hydrogen peroxide, t-butyl hydroperoxide, lauryl peroxide, benzoyl peroxide, dicumyl peroxide, acetyl peroxide, caprylyl peroxide, di-tertbutyl peroxide, diisopropyl percarbonate and dicyclohexyl percarbonate; peracid such as perchlorates; peresters; percarbonates; cerium ammonium nitrate; and the like

[0036] The traceable polymeric viscosifier may be prepared by conventional aqueous polymerization, water-in-oil dispersion polymerization, or solution polymerization where the monomers are polymerized in a suitable solvent employing a suitable free-radical initiator.

[0037] The traceable phosphinate and/or phosphonate moieties may be present in the traceable polymeric viscosifier at an amount of less than 5%weight based on total weight of the polymeric viscosifier. In other embodiments, the phosphinate and/or phosphonate moieties may be at about 0.1% to about 20% weight based on total weight of the polymeric viscosifier.

[0038] The weight average molecular weights of the traceable polymeric viscosifier may be determined by light scattering analysis using known polyacrylamide standards or by intrinsic viscosity measurement. The traceable polymeric viscosifier may have a weight average molecular weight of about 1 million to about 20 million. In some embodiments, the traceable polymeric viscosifier may have weight average molecular weight of about 5 million to about 10 million.

[0039] The traceable polymeric viscosifier may provide enhanced EOR efficiency due to its low mobility compared to petroleum, show reduced sensitivity towards salts presented in the oilfield environment, as well as exhibit improved mechanical stability and other desirable rheological properties found useful in the enhanced oil recovery processes. Moreover, the traceable polymeric viscosifier may have improved chemical and thermal stability under harsh conditions of downhole environment (i.e., high salt concentrations, presence of multivalent ions, elevated temperatures, and extreme pressures).

[0040] A particular embodiment of the method of recovering petroleum from subterranean petroleum-bearing deposit may include injecting an aqueous solution into an oil-bearing formation through at least one injection well to displace the oil from the injection well to at least one production well, wherein the aqueous solution comprises a traceable polymeric viscosifier including a viscosifying moiety and a traceable

phosphinate and/or phosphonate moieties, the viscosifying moiety comprising partially hydrolyzed amide functionality.

[0041] The amount of the traceable polymeric viscosifier in the injection water may be varied depending many factors including, but not limited to, the structure of
5 traceable polymeric viscosifier, the type of subterranean deposit, the level of salts in the injection water, the operating temperature, and the like. In one embodiment, the injection water may comprise the traceable polymeric viscosifier in a concentration range of about 1,500 ppm to about 4,000 ppm based on total weight of the injection water.

[0042] An amount of the traceable polymeric viscosifier added into the injection
10 water may be such that a desired viscosity of the injection water may be obtained. In one embodiment, the injection water may comprise the traceable polymeric viscosifier in an amount that causes the mobility of the aqueous solution to be about 2 to 5 times smaller than the mobility of the oil. The viscosity of aqueous solution may not be too high, since the pressures required to make such solution flow through the reservoir may exceed the
15 fracture pressure of the rock.

[0043] The viscosity of injection water-based solution injected into the injection well may be maintained substantially constant over the period of time required to force the petroleum out of the reservoir and into the production well. The traceable polymeric scale inhibitor may be added to the injection water during EOR applications periodically,
20 continually or continuously to maintain the desired viscosity of the injection water.

[0044] The method of recovering petroleum from subterranean petroleum-bearing deposit may be used to treat the wells at temperatures a temperature range of about 25°C to about 95°C, during tertiary oil recovery, especially in the presence of mineral water containing divalent salts without substantial accompanying break-down of polymer
25 viscosity.

[0045] A particular embodiment of the method of detecting an advancement of water injection through oil reservoir during enhanced oil recovery application may comprise applying an injection water comprising a traceable polymeric viscosifier to the oil reservoir under pressure to force the oil to a production well, the traceable polymeric
30 viscosifier including a viscosifying moiety and a traceable phosphinate and/or phosphonate moieties; taking a sample of reservoir fluid; and measuring a concentration of the traceable phosphinate and/or phosphonate moieties in the reservoir fluid sample to determine an advancement of the water injection through the oil reservoir.

[0046] The amount of traceable polymeric viscosifier in the oilfield fluids may be measured periodically, continually or continuously. Any quantitative technique suitable for determining an amount of phosphinate and/or phosphonate moieties on the traceable polymeric viscosifier may be used including, but not limited to, visually titrating the traceable polymeric viscosifier with a color-forming agent that provides a distinguish and reliable end point, or titrating the traceable polymeric viscosifier with a color-forming agent using colorimeter to determine an end point.

[0047] The presence of divalent salts and/or the temperature of the deposits, which usually contributes significantly to the viscosity breakdown of the polymeric viscosifiers, may not materially affect the traceable polymeric viscosifier.

[0048] In addition to the traceable polymeric viscosifier, the injection water may comprise other viscosifiers, surfactants, solvents, salts, biocides, oxygen scavengers, wax inhibitors, asphaltene inhibitors or other oilfield chemicals if they are compatible with the traceable polymeric viscosifier and do not cause any negative effect or breakdown of the polymeric viscosifier.

[0049] The following Examples are meant to illustrate, but in no way limit, the claimed invention.

EXAMPLES

[0050] Synthesis of Polymeric Samples

[0051] EXAMPLE 1

[0052] Into a round bottomed flask equipped with reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 199.3 g of deionized water and 2.07 g of High Molecular Weight PAM. While introducing nitrogen into the flask, the temperature was increased to 68°C. Then, 20.0 ml of a 1.00% phosphorous acid solution was added. The mixture was stirred for two hours at temperature. The resulting polymer was dried and collected. Polymer was detectable by titration down to 62 ppm, as shown in Figure 1. The viscosity profiles of the untagged polymer and the tagged polymer with different concentrations of tag are shown in Figure 2. The tag changes the viscosity of the polymer, especially at low shear rates. The amount of tag affects the change in viscosity. Low amounts of tag added (0.05 g) increase the viscosity of the polymer, whereas amounts higher than 0.1 g of tag decrease the viscosity. This decrease is not high enough to make the tagged polymer unsuitable to be used as a viscosifier in a chemical EOR application.

[0053] EXAMPLE 2

[0054] Into a round bottomed flask equipped with an addition funnel, reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 340 g deionized water, 8.2g glacial acrylic acid, 24.4g acylamine, and 6mg of iron(II)sulfate.

- 5 This mixture was stirred and degassed for 1 hour at room temperature. A 0.03wt % solution of sodium persulfate was added dropwise. When a change in temperature of 6°C was observed 16mg of sodium hypophosphite was added. The reaction was allowed to proceed for two hours upon which time 9.1g of 50% sodium hydroxide was added.

[0055] Polymer Properties.

- 10 **[0056]** TABLE 1 shows some physical properties of the traceable polymeric species (Examples 1 and 2) and a High Molecular Weight PolyAcrylamide (PAM). The weight average molecular weight ($\overline{M}_w$) and polydispersity index (PDI) of the polymeric samples were determined using Zetasizer Nano series light scattering available from Malvern Instruments. The polymer parameters, radius of gyration, Rg, etc. were
- 15 determined from polyacrylamide standards available from American Polymer Standards.

TABLE 1

Example	Rg	% Charge	$\overline{M}_w \times 10^6$, Daltons
1	61-95 nm	35	3.5-8.5
2	61-95 nm	25	3.5 – 8.5
High Molecular Weight PAM	45-95 nm	35	1.8 – 8.5

Determination of Traceable Efficiency by Titration

- 20 **[0057]** The traceable efficiency of the traceable viscosifier was determined by a micro titration technique based on Palintest Organophosphonate test using Palintest Direct-Reading Titration, Palintest Organophosphonate No 1 Tablet (i.e., indicator tablet), and Palintest Organophosphonate No 2 Solution (i.e., standard thorium nitrate solution), available from Palintest USA.
- 25 **[0058]** The tested traceable viscosifier of known concentration was dissolved in 10 ml of water. To 10 ml of the traceable scale inhibitor solution, one indicator tablet was added, crushed and mixed to dissolve in the solution to produce a solution having

green color. The indicator tablet contained a screened xylene orange indicator together with a buffer mixture which provided the correct conditions for the test. Furthermore, the indicator tablet eliminated the tedious pH correction procedure and ensured an improved green to purple end point color change. A standard thorium nitrate solution in a graduated syringe was added one drop at a time to the tested green solution containing traceable scale inhibitor and indicator, while the tested solution was shaken to ensure an adequate mixing. The standard thorium nitrate solution was added until the end point was reached, which was when the color of the tested solution changed from green to purple. The amount of thorium nitrate solution used corresponded to the amount of traceable phosphinate moiety present in the tested solution in ppm.

[0059] Before the end point, thorium in the standard thorium nitrate solution formed a complex with the traceable phosphinate moiety in the tested solution. The thorium-phosphinate complex was colorless; therefore, there was no change in color of the tested solution. At the end point, the amount of thorium was equal to the amount of traceable phosphinate moiety. After the end point, thorium formed a complex with the indicator in the tested solution, resulting in a purple solution. The thorium-indicator complex occurred only when thorium had formed a complex with all phosphinate moiety present in the tested solution.

[0060] The amounts of standard thorium nitrate solution at the end point of Palintest Organophosphonate titration was used to determine the amounts of traceable phosphinate scale inhibitor present in the tested solution. A linear relationship between the concentration of standard thorium nitrate solution used at the end point and the concentrations of traceable phosphinate scale inhibitor in the tested solution was as shown in Figure 2 and the following formula:

[0061]
$$\text{Conc. of Traceable viscosifier} = [57.5 \times \text{ppm of Thorium Titrant added}] + 51.6 \text{ ppm}$$
 of thorium titrant added is indicated on the graduated syringe, included with the test kit, at the end of the titration.

[0061] Viscosity Measurements

[0062] Viscosity measurements were performed with an Anton Paar MCR-302 rheometer using a cone and plate geometry. All measurements were done at 15°C covering a shear rate range between 0.1 to 1,000 sec⁻¹. All samples were preconditioned by shearing them at 2,000 sec⁻¹ for 5 minutes. The polymer concentration used was 3,000 ppm of polymer in tap water. The tap water was sparged with Nitrogen to eliminate the

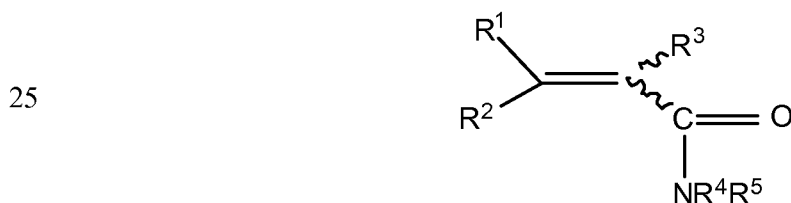
oxygen in the water and the dry polymer was slowly added to it under mild agitation with a magnetic stir bar. This procedure was done under constant sparging with Nitrogen. After all the polymer was added, the solution was left with mild agitation under a blanket of Nitrogen for 3 days in a closed glass container.

- 5 **[0063]** While the invention has been described by reference to various specific embodiments, it should be understood that numerous changes may be made within the scope of the inventive concepts described. Accordingly, it is intended that the invention not be limited to the described embodiments, but will have full scope defined by the language of the following claims.

10

CLAIMS

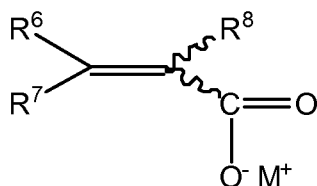
1. A traceable polymeric viscosifier comprising:
 - a viscifying moiety comprising amide functionality; and
 - a traceable moiety selected from the group consisting of phosphinate
- moieties, phosphonate moieties and a combination thereof.
2. The traceable polymeric viscosifier of claim 1 derived from a mixture comprising:
 - a compound selected from the group consisting of hypophosphite,
 - inorganic phosphinate salts, organic phosphinate salt, an amide phosphonate monomer
 - and combinations thereof; and
- an amide monomer capable of being at least partially hydrolyzed.
3. The traceable polymeric viscosifier of claim 1, wherein the amide monomer includes a monomer selected from the group consisting of vinylacrylamide, N-substituted acrylamide, N,N-substituted acrylamide, and combinations thereof.
4. The traceable polymeric viscosifier of claim 1, wherein the viscifying moiety comprising amide functionality and at least one of carboxylate functionality and sulfonate functionality.
5. The traceable polymeric viscosifier of claim 4 derived from a mixture comprising:
 - a compound selected from the group consisting of hypophosphite,
 - inorganic phosphinate salts, organic phosphinate salt, amide phosphonate monomer and
 - combinations thereof;
- an amide monomer represented by structure (I)



wherein R¹, R², R³, R⁴ and R⁵ are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, or a phosphonate group; and
30 a carboxylate monomer represented by structure (II)

(II)

5



wherein R^6 , R^7 and R^8 are independently hydrogen, an alkyl group having up to 7 carbon atoms, or a hydroxyl group; and M is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ where R_1 , R_2 , R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbon atoms.

6. The traceable polymeric viscosifier of claim 5, wherein the amide monomer includes a monomer selected from the group consisting of vinylacrylamide, N-substituted acrylamide, N,N-substituted acrylamide, and combinations thereof.

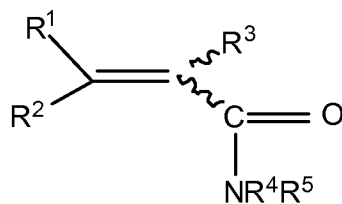
15 7. The traceable polymeric viscosifier of claim 5, wherein the carboxylate monomer includes a member selected from the group consisting of monocarboxylic acid monomers, dicarboxylic acid monomers, anhydrides of cis-dicarboxylic acids, and combinations thereof.

8. The traceable polymeric viscosifier of claim 4 derived from a mixture comprising:
20 a compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, amide phosphonate monomers and combinations thereof;

an amide monomer represented by structure (I)

(I)

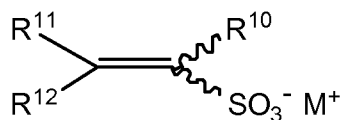
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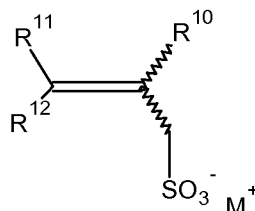
30 wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, or a phosphonate group; and

a sulfonate monomer represented by a structure selected from the group consisting of structure (III), structure (IV), and combinations thereof

(III)



(IV)



5

wherein R^{10} , R^{11} and R^{12} are independently hydrogen, an alkyl group having up to 7 carbon atoms, or a hydroxyl group; M is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $NR_1R_2R_3R_4$ where R_1 , R_2 , R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy group having from 1 to 7 carbon atoms, or a phosphonate group.

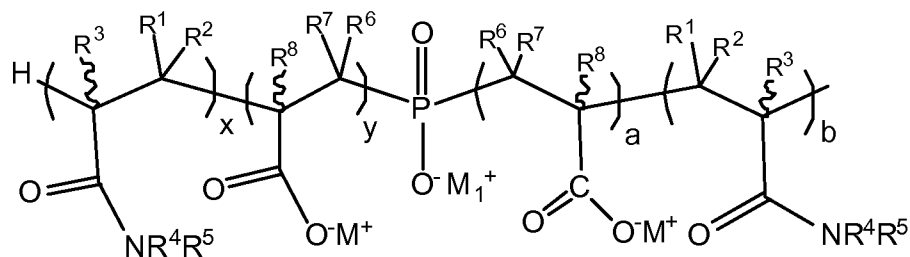
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9. The traceable polymeric viscosifier of claim 8, wherein the sulfonate monomer includes a member selected from the group consisting of vinyl sulfonate, 2-sulfoethyl methacrylate, 2-acrylamido-2-methylpropane sulfonate, styrene sulfonate, and salts thereof.

15

10. The traceable polymeric viscosifier of claim 1, comprising structure (VI):

(VI)



20

wherein

R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy

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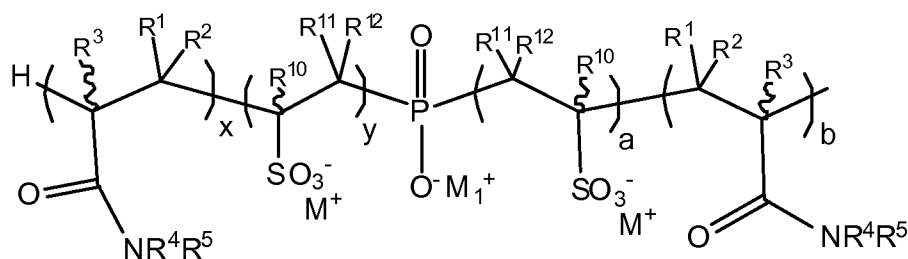
group having from 1 to 7 carbon atoms, or a phosphonate group;

M and M₁ are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or NR₁R₂R₃R₄ where R₁, R₂, R₃ and R₄ are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbon atoms;

x and y are independently integral numbers, a sum of x plus y being greater than 2; and

a and b are independently integral numbers, a sum of a plus b being greater than 2.

- 10 11. The traceable polymeric viscosifier of claim 1 comprising structure (VII)
(VII)



wherein

- 15 R¹, R², R³, R⁴, R⁵, R¹⁰, R¹¹ and R¹² are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, or NR₁R₂ where R₁ and R₂ are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxyl group having from 1 to 7 carbon atoms, or a phosphonate group;

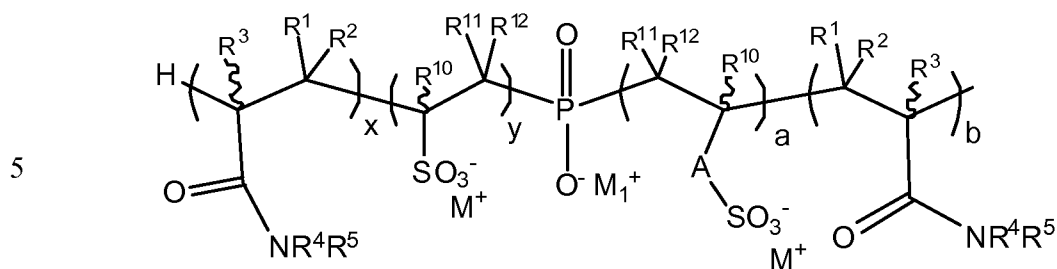
- 20 M and M₁ are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or NR₁R₂R₃R₄ where R₁, R₂, R₃ and R₄ are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbon atoms;

x and y are independently integral numbers, a sum of x plus y being greater than 2; and

a and b are independently integral numbers, a sum of a plus b being greater than 2.

- 25 12. The traceable polymeric viscosifier of claim 1, comprising structure (VIII)

(VIII)



wherein

$R^1, R^2, R^3, R^4, R^5, R^{10}, R^{11}$ and R^{12} are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy group having from 1 to 7 carbon atoms, or a phosphonate group;

M and M_1 are independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, or $NR_1R_2R_3R_4$ where R_1, R_2, R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbon atoms;

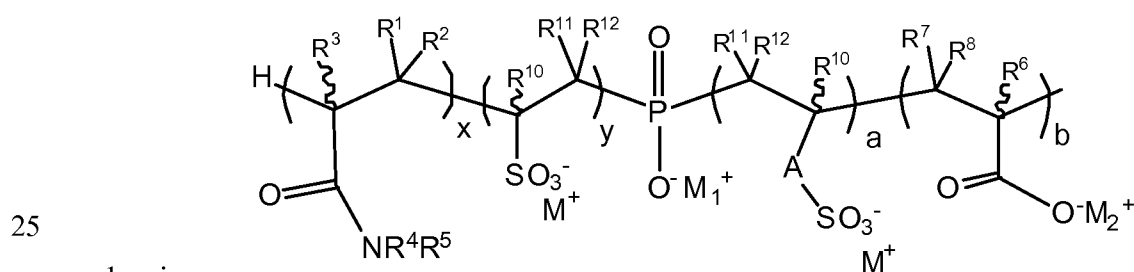
x and y are independently integral numbers, a sum of x plus y being greater than 2; and

a and b are independently integral numbers, a sum of a plus b being greater than 2.

13. The traceable polymeric viscosifier of claim 1, comprising structure (IX)

20

(IX)



wherein

$R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^{10}, R^{11}$ and R^{12} are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, or NR_1R_2 where R_1 and R_2 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, an alkoxy group having from 1 to 7 carbon atoms, or a phosphonate group;

M, M_1 and M_2 are independently hydrogen, an alkali metal, an alkaline earth

metal, ammonium, or $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$ where R_1 , R_2 , R_3 and R_4 are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbon atoms;

5 x and y are independently integral numbers, a sum of x plus y being greater than 2; and

a and b are independently integral numbers, a sum of a plus b being greater than 2.

14. The traceable polymeric viscosifier of claim 1, wherein an amount of the traceable moiety is less than about 5% weight based on a total weight of the traceable polymeric viscosifier.

10 15. The traceable polymeric viscosifier of claim 1, wherein an amount of the traceable moiety is from about 0.1% to about 20% weight based on a total weight of the traceable polymeric viscosifier.

16. The traceable polymeric viscosifier of claim 1, having a weight average molecular weight from about 1 million to about 20 million.

15 17. An aqueous solution for an enhanced oil recovery process, the aqueous solution including a traceable polymeric viscosifier of claim 1.

18. The aqueous solution of claim 17, wherein an amount of the traceable polymeric viscosifier in the aqueous solution is from about 1,500 ppm to about 4,000 ppm.

20 19. The aqueous solution of claim 17, wherein a mobility of the aqueous solution is about 2 to 5 times smaller than a mobility of the oil.

20. The aqueous solution of claim 17, further comprising a chemical selected from the group consisting of surfactants, solvents, salts, biocides, oxygen scavengers, wax inhibitors, asphaltene inhibitors, and combinations thereof.

25 21. An aqueous solution for an enhanced oil recovery process, the aqueous solution including a traceable polymeric viscosifier of claim 4.

22. A method of recovering petroleum from a subterranean oil-bearing deposit, the method comprising:

 injecting an aqueous solution into a deposit area through at least one injection well to cause oil to flow from the deposit area to at least one production well,
30 wherein the aqueous solution comprises a traceable polymeric viscosifier including a traceable moiety selected from the group consisting of a phosphinate moiety, a phosphonate moiety and a combination thereof, and a viscosifying moiety comprising amide functionality.

23. The method of claim 22, wherein the viscosifying moiety comprises amide functionality and at least one of carboxylate functionality and sulfonate functionality.
24. The method of claim 22, wherein the aqueous solution has a mobility of about 2 to 5 times smaller than a mobility of the oil.
- 5 25. The method of claim 22, wherein injecting an aqueous solution into deposit area comprises:
- applying an injection water comprising a traceable polymeric viscosifier to the oil reservoir under pressure;
 - taking a sample of reservoir fluid; and
 - 10 measuring a concentration of the traceable moiety in the reservoir fluid sample to determine an advancement of the water injection through the oil reservoir.

FIG. 1

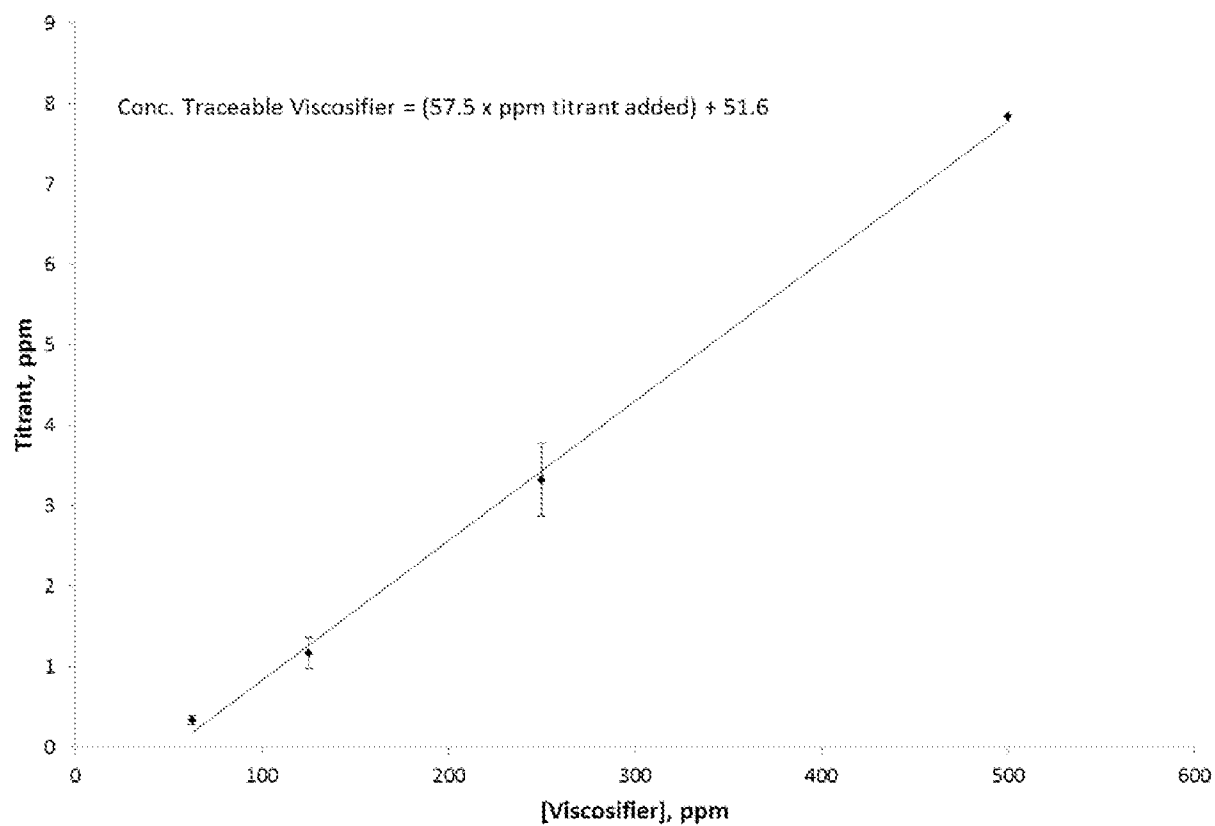
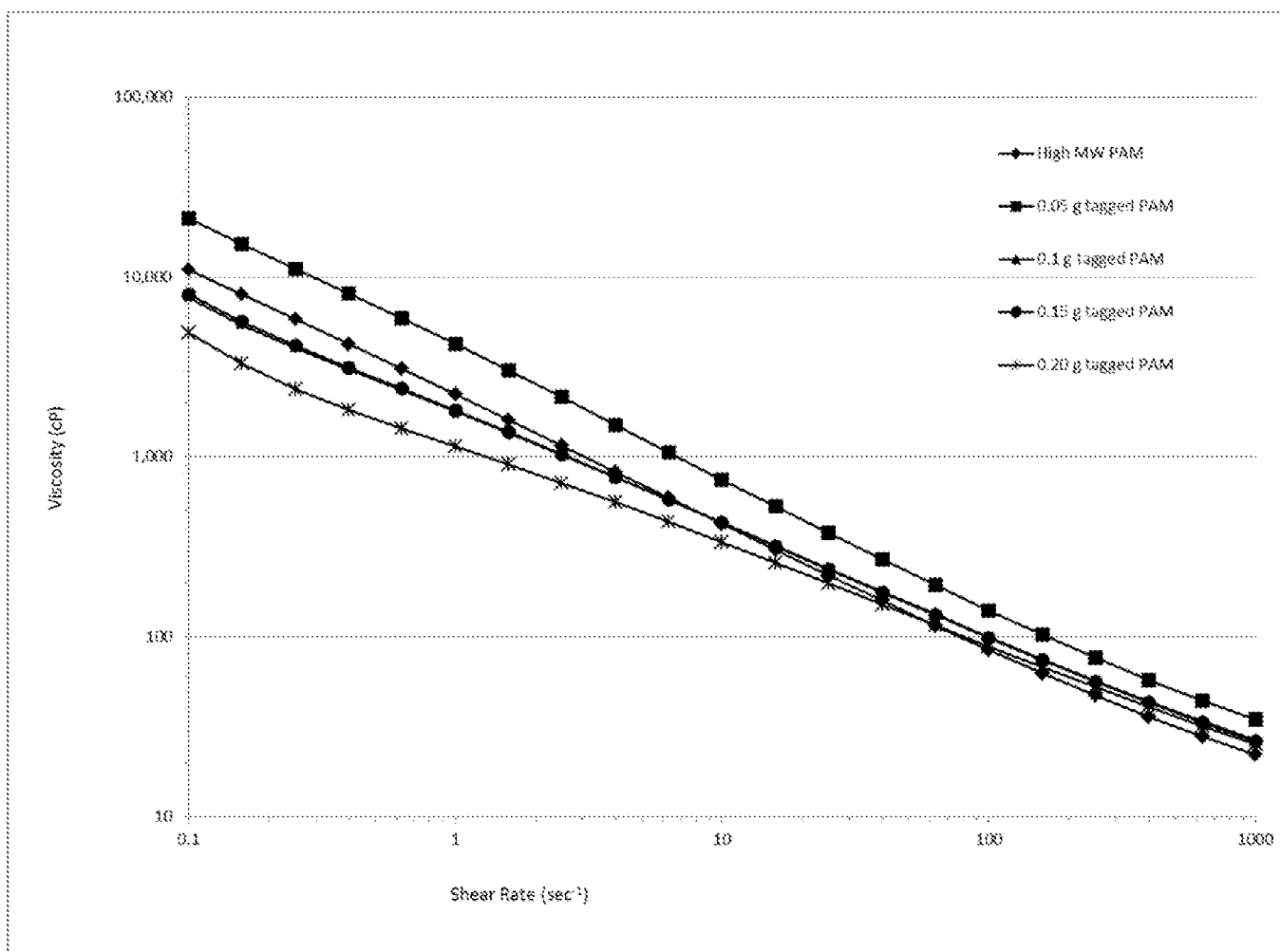


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/062135

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/588 C02F5/14 C08F30/02 D06M15/356
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 C02F C08F D06M

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

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

EPO-Internal, 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 2012/006551 A1 (CARMAN PAUL S [US] ET AL) 12 January 2012 (2012-01-12) paragraphs [0011], [0013]; claim 1 the whole document -----	1-25
X	US 2012/202958 A1 (LIU ZHAOQING [CN] ET AL) 9 August 2012 (2012-08-09) paragraph [0026]; claim 1; example 3 the whole document -----	1-25
X	US 2003/109385 A1 (GUNN ALISTAIR MANSON [GB] ET AL) 12 June 2003 (2003-06-12) paragraphs [0001], [0002]; claims 1-4 the whole document ----- -/-	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

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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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

14 January 2014

Date of mailing of the international search report

21/01/2014

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/062135

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/100665 A2 (RHODIA OPERATIONS [FR]; TALINGTING PABALAN RUELA [US]; MARTINEZ-CASTRO) 18 August 2011 (2011-08-18) paragraphs [0207], [0220], [0263], [0764] - [0774] the whole document -----	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/062135

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US 2012202958	A1	09-08-2012	CN 102596976 A 18-07-2012 EP 2493904 A1 05-09-2012 JP 2013509355 A 14-03-2013 KR 20120095940 A 29-08-2012 US 2012202958 A1 09-08-2012 WO 2011050534 A1 05-05-2011
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