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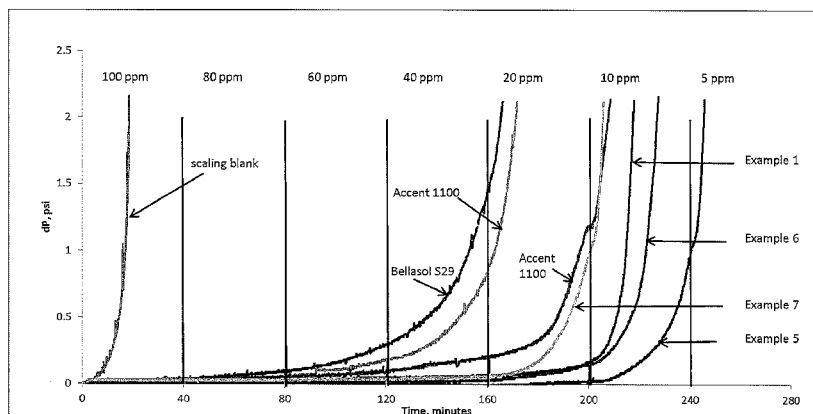
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(54) Title: TRACEABLE POLYMERIC SULFONATE SCALE INHIBITORS AND METHODS OF USING

FIG. 1

(57) **Abstract:** A traceable polymeric scale inhibitor comprises a traceable phosphinate moiety and a scale inhibiting moiety including sulfonate functionality. The traceable polymeric scale inhibitor may be used for oilfield applications. A method of reducing scale formation comprises treating the fluid subjected to scale formation with the traceable polymeric scale inhibitor. The method provides a means to determine when additional treatment of scale inhibitors is needed, which conduit or wellbore needs additional treatment of scale inhibitor, and how much additional scale inhibitor is needed in the repeat treatment to provide effective inhibition of scale formation.

## TRACEABLE POLYMERIC SULFONATE SCALE INHIBITORS AND METHODS OF USING

### FIELD OF THE INVENTION

5           **[0001]** Embodiments of the present disclosure relate to traceable polymeric scale inhibitors and to methods of using such inhibitors for reducing scale formation.

### BACKGROUND OF THE DISCLOSURE

**[0002]** The precipitation of inorganic salts, such as calcium carbonate, calcium sulfate, barium sulfate or strontium sulfate, from aqueous fluids to form scale is a  
10   persistent and common problem encountered in oilfield operations to recover hydrocarbons from subterranean formations. Scale formation in the subterranean formations, oilfield production equipment and tubing can be initiated by a variety of factors including, for example, pressure, pH, temperature, turbulence, surface characteristics, or mixing of incompatible fluids which frequently happens during water  
15   flooding steps of enhanced oil recovery (EOR) operations. The presence of carbon dioxide in the formations further exacerbates scaling problems. Carbon dioxide is frequently introduced into the formations during EOR operations resulting in absorption of carbon dioxide into aqueous fluids. As aqueous fluids enter wellbore during production, a reduction in pressure causes the absorbed carbon dioxide to flash out of the  
20   aqueous fluids to gas phase. This increases the pH of aqueous fluids and causes growth of calcium carbonate scales in the production wellbore as well as in the production tubing and equipment.

**[0003]** The scale formation affects heat transfer, interferes with fluid flow, facilitates corrosion and harbors bacteria. In oilfield piping and tubing, scale can cause  
25   restriction to flow and high friction loss. Scale formation in oilfield operations is an expensive problem causing delays and shutdowns for cleaning and removal.

**[0004]** The scale deposited in subterranean formations or production equipment and tubing may be removed mechanically or chemically, both of which are ineffective, costly and time-consuming. The wellbore must be shut-in during cleaning operation. For  
30   chemical removal methods, chemical agents are repeatedly injected into the affected formations, equipment or tubing to attack the scale. Chemical removal methods include acid treatments, base treatments, two stage treatments (bases followed by acids), or chelating treatments such as using EDTA (ethylenediaminetetraacetic acid) as chelant.

For mechanical removal methods, scale may be removed using various mechanical devices such as impact or cavitation jets.

[0005] Preventative methods for inhibiting the growth and deposition of scale have been considered as more preferred approach to the problem of scale formation. The most common classes of scale inhibitors are inorganic phosphates, organophosphorus compounds and organic polymers. The inorganic phosphates are sodium tripolyphosphate and hexametaphosphate. Organophosphorus compounds are phosphonic acid and phosphate ester salts. The organic polymers used are generally low molecular weight acrylic acid salts or modified polyacrylamides and copolymers thereof.

[0006] The scale inhibitor may be added directly to the fluid being treated, such as to the aqueous fluids present in the subterranean formations, or in surface or subsurface tubing in fluid communication therewith. Alternatively, the scale inhibitor may be applied to the subterranean formations by means of "squeeze treatment." In the squeeze application, the oilfield production is halted while the scale inhibitor is injected into the subterranean formations. The wellbore is shut in for a suitable period and then returned to production. During the shut-in period, the scale inhibitor adsorbs to the formation matrix by temperature-activated precipitation or precipitates within the formation when applied as a precipitation squeeze. When the wellbore is put back into production, the scale inhibitor leaches out of the formation into the aqueous fluids at sufficiently high concentrations to prevent scale formation.

[0007] The scale inhibitor sufficiently controls scale formation only when its concentration in the fluids is above or equal to its minimum inhibitor concentration (MIC). During oil production, after a squeeze application, the concentration of scale inhibitor in the oilfield fluids will diminish over time until such time that the concentration of scale inhibitor is at about or below the MIC level. Once the concentration of scale inhibitor falls below the MIC level, the scale inhibitor can no longer effectively prevent scale formation. Additional scale inhibitor must be added such that the concentration of scale inhibitor in the fluids is maintained above the MIC level. Therefore, it is desirable to know the concentration of scale inhibitor in the oilfield fluids and properly determine when and how much additional scale inhibitor must be added into the oilfield fluids to effectively prevent scale formation. It has been difficult to determine when and how much additional scale inhibitor is needed, and which conduit or wellbore requires additional scale inhibitor because the amount of scale inhibitor in the oilfield

fluids is very low, generally in parts per million (ppm) levels. To address this difficulty, scale inhibitors have been tagged or labeled so that it may be readily detected and residuals quickly quantified.

5       **[0008]** European Patent Application No. 157465 A1, published on September 10, 1985, to Bevaloid Limited, discloses polymer compositions for water treatment having activated groups attached to the polymer chain backbone by carbon-carbon bonds. The activated groups are subjected to color forming reaction with diazonium aromatic compounds, thereby enabling the polymer compositions to be detected at very low concentration in water.

10       **[0009]** U.S. Patent No. 7,943,058, issued on May 17, 2011 to Rhodia Operations, discloses scale inhibitors incorporating certain marking atoms such as phosphorous, boron, silicon, germanium and the like so that the concentration of scale inhibitors may be determined by inductively coupled plasma (ICP) analysis for the marking atoms.

15       **[0010]** U.S. Patent Publication No. 2012/0032093 A1, published on February 9, 2012 to Kemira Chemicals Incorporation, discloses scale inhibitor compositions including a scale inhibiting moiety and a traceable imidazole moiety. The imidazole moiety provides fluorescence at a wavelength of about 424 nm, and therefore its concentration may be determined using fluorescence spectroscopy technique.

#### SUMMARY OF THE DISCLOSURE

20       **[0011]** In some embodiments, a traceable polymeric scale inhibitor includes a scale inhibiting moiety and a traceable phosphinate moiety, wherein the scale inhibiting moiety comprises sulfonate functionality. In one embodiment, a traceable polymeric scale inhibitor includes a scale inhibiting moiety and a traceable phosphinate moiety, wherein the scale inhibiting moiety comprises sulfonate functionality and carboxylate  
25       functionality.

**[0012]** In other embodiments, a method of reducing scale formation includes treating fluids subjected to scale formation with a traceable polymeric scale inhibitor, wherein the traceable polymeric scale inhibitor comprises a scale inhibiting moiety and a traceable phosphinate moiety, the scale inhibiting moiety comprising sulfonate  
30       functionality. In one embodiment of such method, the scale inhibiting moiety comprises sulfonate functionality and carboxylate functionality.

**[0013]** In one particular embodiment, a method of reducing scale formation in oilfield operations includes adding the traceable polymeric scale inhibitor to the oilfield

fluids such as produced water or injection water during secondary recovery processes. In one particular embodiment, a method of reducing scale formation in oilfield operations includes squeeze applying such traceable polymeric scale inhibitor to the subterranean formations.

- 5           **[0014]** Certain embodiments relate to a method of maintaining a desired amount of a traceable polymeric scale inhibitor in an aqueous fluid system to effectively reduce scale formation. The method comprises adding the traceable polymeric scale inhibitor to the aqueous fluid system, the traceable polymeric scale inhibitor comprising a traceable phosphinate moiety and a scale inhibiting moiety comprising sulfonate functionality;
- 10       determining a concentration of the traceable phosphinate moiety in the aqueous fluid system; converting the concentration of the traceable phosphinate moiety to a concentration of the traceable polymeric scale inhibitor in the aqueous fluid system; and adjusting the concentration of the traceable polymeric scale inhibitor according to what the desired concentration is for the traceable polymeric scale inhibitor in the aqueous
- 15       fluid system.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- [0015]** Fig. 1 shows the comparative barium sulfate brine dynamic scale loop (DSL) or tube blocking test results of the traceable polymeric scale inhibitor of Example 1 and three commercially available polymeric scale inhibitors Bellasol S29 (PPCA),
- 20       Accent 1100 and Accent 1121.

**[0016]** Fig. 2 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 scale inhibitor.

#### DESCRIPTION OF THE DISCLOSURE

- 25           **[0017]** 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,
- 30       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.

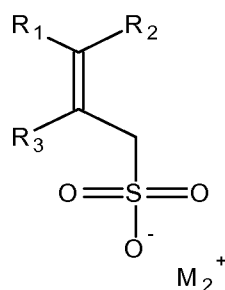
**[0018]** In a particular embodiment, a traceable polymeric scale inhibitor may comprise a scale inhibiting moiety including sulfonate functionality, and a traceable

phosphinate moiety. It is understood that the traceable moiety may also prevent scale formation. Furthermore, the scale inhibiting moiety may be detectable.

[0019] The traceable polymeric scale inhibitor may be prepared from a mixture comprising: an allylsulfonate-based monomer; and a phosphinate compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, and combinations thereof.

[0020] The term "allyl sulfonate-based monomer" includes a compound represented by structure (I):

(I)



10

wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group; and  $\text{M}_2$  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  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxyl group having from 1 to 7 carbons.

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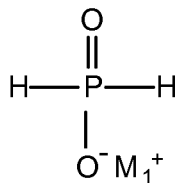
[0021] Various monomers with the represented structure (I) may be used including, but not limited to, vinyl sulfonic acid, vinyl sulfonate, allylsulfonic acid, styrene sulfonic acid, sodium styrene sulfonate, allyloxy benzenesulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, or salts thereof such as sodium, potassium and ammonium salts.

20

[0022] Phosphinate compounds may be represented by structure (II):

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(II)



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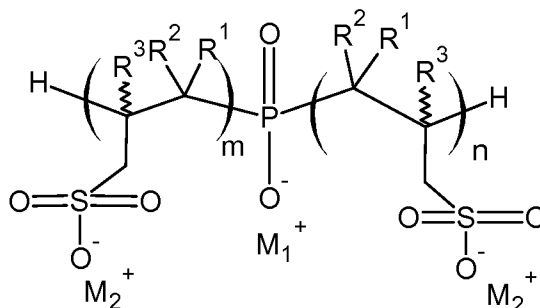
wherein  $\text{M}_1$  is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $\text{NR}_1\text{R}_2\text{R}_3\text{R}_4$  where  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons.

10 [0023] Various phosphinate compounds with the represented structure (II) may be used including, but not limited to, hypophosphite, inorganic phosphinate salts, organic phosphinate salt, or combinations thereof.

[0024] In one embodiment, the traceable polymeric scale inhibitor may comprise structure (III):

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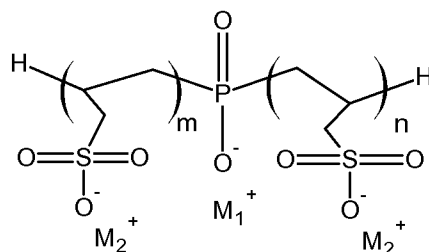
(III)



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group;  $m$  and  $n$  are independently integral numbers; a sum of  $m$  plus  $n$  is greater than 2; and  $\text{M}_1$  and  $\text{M}_2$  are independently 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  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons.

25 [0025] In one embodiment, the traceable polymeric scale inhibitor may comprise structure (IV):

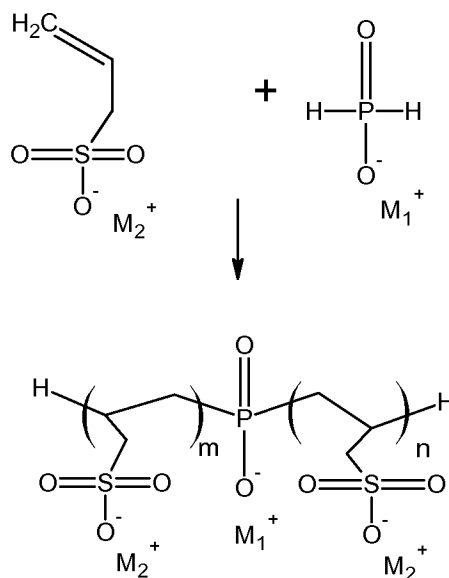
(IV)



wherein m and n are independently integral numbers; a sum of m plus n is greater than 2; and  $M_1$  and  $M_2$  are independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons.

[0026] In one embodiment, the disclosed traceable polymeric scale inhibitor may comprise the polymer prepared from vinyl sulfonate and phosphinate salt by a polymerization process, as shown in Formula (V):

(V)

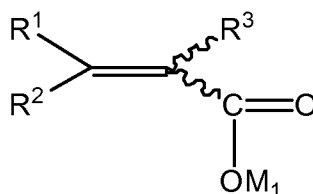


[0027] In one embodiment, the traceable polymeric scale inhibitor may comprise a traceable phosphinate moiety and a scale inhibiting moiety including sulfonate functionality and carboxylate functionality.

[0028] The traceable polymeric scale inhibitor 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 allyl sulfonate-based monomer represented by structure (I); and a  
 5 monocarboxylate monomer, or a dicarboxylate monomer

[0029] The term "monocarboxylate monomer" includes a compound represented by structure (VI):

(VI)

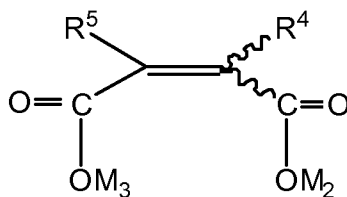


wherein  $R^1$ ,  $R^2$  and  $R^3$  are independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl groups; and  $M_1$  is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  where  $R_1$ ,  
 15  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxyl group having from 1 to 7 carbons.

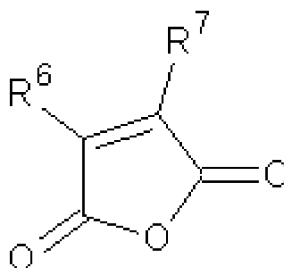
[0030] The monocarboxylate monomers represented by structure (VI) may include, but are not limited to, carboxylic acid monomers such as acrylic acid, oligomeric acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid and the water-soluble salts  
 20 thereof.

[0031] The term "dicarboxylate monomer" includes a compound represented by structure (VII) or (VIII):

(VII)



(VIII)



wherein  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are independently hydrogen, an alkyl group containing up to 7 carbon atoms, or hydroxyl group;  $M_2$  and  $M_3$  are independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and

5  $NR_1R_2R_3R_4$  where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons.

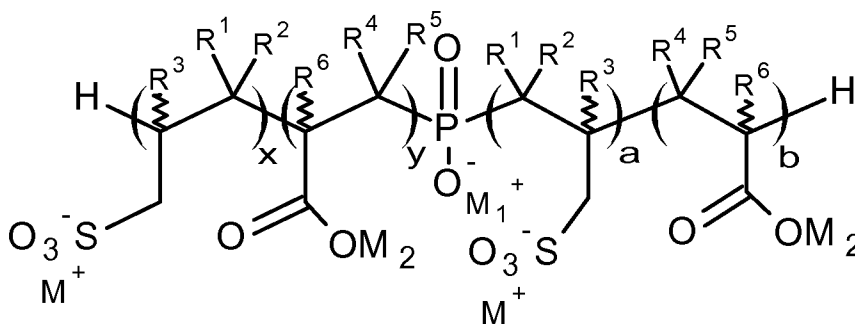
[0032] Carboxylate monomers represented by structure (VIII) may include, but are not limited to, monocarboxylic acid monomers such as acrylic acid, oligomeric acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid and the water-soluble salts thereof;

10 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

15 acid; cyclohexenedicarboxylic acid; cis-1,2,3,6-tetrahydrophthalic anhydride; 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride; and water-soluble salts thereof.

[0033] In one embodiment, the traceable polymeric scale inhibitor may comprise structure (IX):

(IX)



20 wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  are independently hydrogen, an alkyl group containing up to 7 carbon atoms, hydroxyl group, carboxylate group or  $NR_1R_2$  where  $R_1$  and  $R_2$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons; and  $M$ ,  $M_1$ ,  $M_2$  each is independently

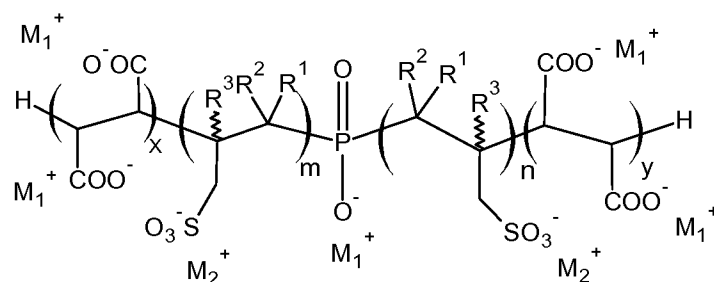
25 selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, an

alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons.

[0034] In one embodiment, the traceable polymeric scale inhibitor may comprise structure (X):

5

(X)



wherein  $R^1$ ,  $R^2$ ,  $R^3$  are independently hydrogen, an alkyl group containing up to 7 carbon atoms, hydroxyl group, carboxylate group or  $NR_1R_2$  where  $R_1$  and  $R_2$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbons; and  $M_1$  and  $M_2$  each is independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or alkoxy group having from 1 to 7 carbons.

[0035] In some embodiments, the traceable polymeric scale inhibitor may be prepared from a mixture comprising: an allyl sulfonate-based monomer, a dicarboxylate monomer represented by structure (VIII), and a phosphinate compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salt, and combinations thereof.

[0036] The traceable polymeric scale inhibitor may be produced by any suitable polymerization process. Those skilled in the art are familiar with various polymerization processes. The proportion of the chemicals (e.g. monomers, initiators, chain transferring agents, 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.

[0037] The polymerization may be carried out in a presence of polymerization 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. The amount of polymerization initiators may be about 1% to about 20% weight based on the total weight of the monomers. After the desired reaction time, the polymerization may be terminated with or without an addition of chain transferring agent, such as methylether hydroquinone or a free radical scavenger such as ascorbic acid. The desired reaction time may vary with reaction temperature, initiator concentration, and degree of polymerization desired.

[0038] The traceable phosphinate moiety may be present in the traceable polymeric scale inhibitor at an amount of no more than about 20% weight based on total weight of the polymeric scale inhibitor. In one embodiment, the phosphinate moiety may be at about 0.01% to about 20% weight based on total weight of the polymeric scale inhibitor. In one embodiment, the phosphinate moiety may be at about 0.1% to about 2% weight based on total weight of the polymeric scale inhibitor.

[0039] The molecular weight of the traceable polymeric scale inhibitor may be determined by means of a size exclusion chromatographic technique employing a polymeric gel packed column. The traceable polymeric scale inhibitor may have a weight average molecular weight of about 800 Daltons to about 15000 Daltons. In other embodiments, the weight average molecular weight may be in a range of about 1000 Daltons to about 7000 Daltons.

[0040] The traceable polymeric scale inhibitor may reduce the scale formation in subterranean formations, in surface or subsurface tubing or equipment in fluid communication with the formations.

[0041] An effective amount of the traceable scale inhibitor against scale formation may vary based on various factors including, but not limited to, the particular system to be treated, the scale inhibiting moieties, the area subjected to scale deposition, water quantity, pH, temperature, or concentration of the scale forming species. In one embodiment, an effective amount of the traceable scale inhibitor (i.e., MIC concentration) may be less than about 50 ppm. In some embodiments, the effective amount may be about 5 ppm to about 20 ppm.

[0042] In a particular embodiment, a method of reducing scale formation may comprise treating fluids subjected to scale formation with a traceable polymeric scale inhibitor, the polymeric scale inhibitor comprising a traceable phosphinate moiety and a scale inhibiting moiety including sulfonate functionality. In one embodiment, the method  
5 of reducing scale formation may comprise treating fluids subjected to scale formation with a traceable polymeric scale inhibitor, the polymeric scale inhibitor comprising a traceable phosphinate moiety and a scale inhibiting moiety including sulfonate functionality and carboxylate functionality.

[0043] Prior to using the traceable scale inhibitor at a field site, experiments may  
10 be conducted in a laboratory to determine an effective minimum inhibitor concentration (MIC) of the traceable scale inhibitor. At the field site, the operators may quickly determine an amount of the scale inhibitor in the tested fluids. By comparing the detected amount of traceable scale inhibitor in the tested fluids with the MIC value of the traceable scale inhibitor, the operators may readily decide when it is most suitable to retreat the  
15 reservoir or to apply additional scale inhibitor, and at which rate and amount the additional scale inhibitor should be added into the fluids.

[0044] In a particular embodiment, a method of reducing scale formation may comprise: adding the traceable polymeric scale inhibitor to the fluids subjected to scale formation; measuring an amount of the traceable polymeric scale inhibitor in the fluids;  
20 and further adding the traceable polymeric scale inhibitor to the fluids when the measured amount of traceable polymeric scale inhibitor is approaching a minimum inhibition concentration (MIC) of the traceable polymeric scale inhibitor. The traceable scale inhibitor may be added directly into the fluid system to be treated in a fixed quantity, or may be provided as an aqueous solution and added periodically, continually, or  
25 continuously to the fluid system as desired.

[0045] In some embodiments, a method of reducing scale formation in oilfield applications may comprise: adding the traceable polymeric scale inhibitor to oilfield fluids; measuring an amount of the traceable polymeric scale inhibitor in the oilfield fluids; and further adding the traceable polymeric scale inhibitor to the oilfield fluids  
30 when the measured amount of traceable polymeric scale inhibitor is approaching a minimum inhibition concentration (MIC) of the traceable polymeric scale inhibitor.

[0046] The traceable polymeric scale inhibitor may be added to the oilfield fluids such as produced water or injection water during secondary recovery processor

periodically, continually or continuously. Furthermore, the traceable polymeric scale inhibitor may be added by squeeze applying to the subterranean formations.

Additionally, the traceable scale inhibitors may be applied by other techniques commonly used offshore including, but not limited to, gas-lift injection, downhole annulus injection, encapsulation or soluble matrix techniques, sub-sea wellhead injection, or secondary topside treatment.

[0047] The amount of traceable polymeric scale inhibitor in the oilfield fluids may be measured periodically, continually or continuously. Any quantitative technique suitable for determining the amount of traceable polymeric scale inhibitor may be used including, but not limited to, visually titrating the traceable polymeric scale inhibitor with a color-forming agent that provides a distinguish and reliable end point, or titrating the traceable polymeric scale inhibitor with a color-forming agent using colorimeter to determine an end point.

[0048] In a particular embodiment, a method of maintaining a desired amount of a traceable polymeric scale inhibitor in an aqueous fluid system may comprise: adding the traceable polymeric scale inhibitor to the aqueous fluid system; determining an amount of the traceable phosphinate moiety in the aqueous fluid system; converting the amount of traceable phosphinate moiety to an amount of the traceable polymeric scale inhibitor in the aqueous fluid system; and adjusting the amount of the traceable polymeric scale inhibitor according to what the desired concentration is for the traceable polymeric scale inhibitor in the aqueous fluid system.

[0049] The traceable polymeric scale inhibitor may be added to the aqueous fluid present in the subterranean formations, in surface or subsurface tubing in fluid communication therewith.

[0050] In one embodiment, the traceable polymeric scale inhibitor may be added into the subterranean formations by squeeze treatment. The wellbore is shut in for a suitable period before being returned to production. During the shut-in period, the traceable scale inhibitor may be adsorbed onto the formation matrix. As the production resumes, the traceable scale inhibitor is desorbed over a period of time into the aqueous fluids to prevent scale formation. Samples of the oilfield fluids may be taken periodically, continually or continuously to determine the amount of traceable phosphinate moiety in the fluids and consequently the amount of the traceable polymeric scale inhibitor. Then, an additional aqueous solution of the traceable scale inhibitors may

be injected (“re-squeezed”) into the formations such that the amount of traceable polymeric scale inhibitor is maintained above the MIC level.

5       **[0051]** In one embodiment, the traceable polymeric scale inhibitor may be added into water injection and/or water production. Samples of the produced and/or formation fluids may be taken periodically, continually or continuously to determine the amount of traceable phosphinate moiety in the fluids and consequently the amount of traceable polymeric scale inhibitor. Then, an additional aqueous solution of the traceable scale inhibitor may be added into the fluids at the amount needed to maintain the concentration of traceable scale inhibitor above MIC level.

10       **[0052]** The traceable polymeric scale inhibitors may exhibit desirable scale reduction properties with respect to calcite, barite and other scales under harsh oilfield production conditions (i.e., high temperature, high ionic strength and low pH environments). Breakdowns, maintenance, cleaning and repairs caused or necessitated by scale formation may be minimized when the traceable polymeric scale inhibitor is used.

15       **[0053]** The traceable polymeric scale inhibitor may effectively reduce scale formation at a lower MIC level than those of known polymeric scale inhibitors. For example, in the squeeze treatment, the concentration of the traceable polymeric scale inhibitor may be dropped to lower levels before a repeat squeeze treatment must be performed, thereby extending the squeeze lifetime beyond that available with known  
20       scale inhibitors.

**[0054]** Moreover, the traceable polymeric scale inhibitor may provide a quick, simple, and reliable means to evaluate when additional treatment of scale inhibitors is needed, which conduit or wellbore needs additional treatment of scale inhibitor, and how much additional scale inhibitor is needed in the repeat treatment to provide effective  
25       inhibition of scale formation. For example, the traceable phosphinate moiety may be detected quantitatively by titration techniques, which may be simple, quick, and reliable for oilfield applications.

**[0055]** In addition to oilfield applications, the traceable scale inhibitor may be used as scale inhibitor in any industrial water system where scale inhibition is needed.  
30       Examples of such industrial water systems may include, but not limited to, cooling tower water systems; boiler water systems; hot water heaters; heat exchangers; mineral process waters; paper mill water systems; black liquor evaporators in the pulp industry; desalination systems; cleaning system; pipelines; gas scrubber systems; continuous

casting processes in the metallurgical industry; air conditioning and refrigeration systems; industrial and petroleum process water; water reclamation and purification systems; membrane filtration water systems; food processing streams; and waste treatment systems.

5           **[0056]** The traceable polymeric scale inhibitor may be used in combination with other water treatment agents, if other agents are compatible with the traceable scale inhibitor and do not cause precipitations of the traceable scale inhibitor. Non-limiting examples of other water treatment agents may include, but are not limited to, viscosification agents; surfactants such as anionic surfactants, non-ionic surfactants and  
10        cationic surfactants; sequestrates; chelating agents; corrosion inhibitors; hydrate inhibitors; anti-agglomeration agents; asphaltene inhibitors wax inhibitors; biocides; bleaches; demulsifiers; foam controlling agents; oxygen scavengers; sulfide scavengers; pH controlling and/or buffering agents; chromium salts; zinc salts; dispersants; coagulants; or combinations thereof.

15           **[0057]** In the squeeze treatment application, the traceable polymeric scale inhibitor may be used in conjunction with spearhead chemicals, surfactants and/or emulsifiers. These chemicals may be applied prior to the squeeze treatment of the traceable polymeric scale inhibitor to aid adsorption onto the rock and to minimize emulsification problems.

20           **[0058]** The following Examples are meant to illustrate, but in no way limit, the claimed invention.

#### EXAMPLES

**[0059]** To determine the scale inhibition efficiency and traceable ability of the traceable polymeric scale inhibitor, various traceable polymers samples were synthesized  
25        as described in the following Examples 1-7 and tested as described below. These included a conventional copolymer (MASAS, without traceable phosphinate moiety) of malic anhydride and sodium allylsulfonate which was synthesized and tested to provide comparative scale inhibition efficiency to the traceable polymeric scale inhibitors.

#### **[0060]**   Syntheses of the Polymeric Samples

30           **[0061]**   EXAMPLE 1

**[0062]**   Into a round bottomed flask equipped with two addition funnels, reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 182.7 g deionized water, 75.6g sodium allylsulfonate (0.5 mol), 48.6g maleic anhydride (0.5 mol)

and 0.72 g (0.0081 moles) sodium hypophosphite. While introducing nitrogen into the flask, the temperature was increased to 100°C. Then, 30.6% sodium persulfate solution was added dropwise through an addition funnel over 2 hours. The molar ratio of the monomers and sodium hypophosphite is 125:1. The addition rate of the persulfate solution was 14 ml/hr. After addition of the reactants was completed, the solution was aged for 1 hour at 80°C and then was left standing for cooling to room temperature. Once cooled, 50% sodium hydroxide solution was added to provide a sodium salt of allylsulfonate/maleic acid /phosphinate copolymer at 40% solids, pH of 4.01 and number average molecular weight of 1352.

10        **[0063]**    EXAMPLE 2

**[0064]**    A comparative example was prepared by the method described in Example 1, without the addition of the sodium hypophosphite. A 16% sodium persulfate solution as added to the reaction mixture at a rate of 9.5 ml/hr. The sodium salt of allylsulfonate/maleic acid co-polymer was obtained having 47% solids, a pH of 4.03 and a number average molecular weight of 1218.

**[0065]**    EXAMPLE 3

**[0066]**    A copolymer phosphinate was prepared except that 94.7g sodium allylsulfonate (0.66 mol), 21.5g maleic anhydride (0.22mol), 0.72g sodium hypophosphite was added to the reaction vessel under the same conditions stated in Example 1. The sodium salt was obtained having 43% solids, a pH of 4.22 and a number average molecular weight of 1772.

**[0067]**    EXAMPLE 4

**[0068]**    A copolymer phosphinate was prepared except that 43.8g sodium allylsulfonate (0.30 mol), 88.5g maleic anhydride (0.90mol), 0.72g sodium hypophosphite was added to the reaction vessel under the same conditions stated in Example 1. The sodium salt was obtained having 44% solids, a pH of 4.11 and a number average molecular weight of 369.

**[0069]**    EXAMPLE 5

**[0070]**    Into a round bottomed flask equipped an addition funnel, reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 259.5 g vinylsulfonic acid solution (25%), 49.3 g maleic anhydride and 0.72 g (0.0081 moles) sodium hypophosphite. While introducing nitrogen into the flask, the temperature was increased to 100°C. Then, 21 % sodium persulfate solution was added dropwise through

an addition funnel over 5 hours. The molar ratio of the monomers and sodium hypophosphite is 101:1. The addition rate of the persulfate solution was 26 ml/hr. After addition of the reactants was completed, the solution was aged for 1 hour at 80°C and then was left standing for cooling to room temperature. Once cooled, 50% sodium hydroxide solution was added to provide a sodium salt of maleic acid /vinylsulfonic acid phosphinate copolymer at 38% solids, pH of 3.97 and number average molecular weight of 750.

**[0071]** EXAMPLE 6

**[0072]** A terpolymer phosphinate was prepared by adding into a round bottomed flask equipped with two addition funnels, reflux condenser, nitrogen inlet, temperature probe, and stirrer, 72.1 g sodium allylsulfonate, 49.1 g maleic anhydride and 0.72 g (0.0081 moles) sodium hypophosphite. While introducing nitrogen into the flask, the temperature was increased to 100°C. Then, 72.2 g of an aqueous solution of 50.5% acrylic acid (AA) and a 22.4% sodium persulfate solution were added simultaneously dropwise through separate addition funnels over 5 hours. The molar ratio of the monomers and sodium hypophosphite is 166:1. The addition rates of the two vessels were: persulfate solution at 53 ml/hr and acrylic acid at 14 ml/hr. After addition of the reactants was completed, the solution was aged for 1 hour at 80°C and then was left standing for cooling to room temperature. Once cooled, 50% sodium hydroxide solution was added to provide a sodium salt of allylsulfonate/acrylic acid /vinylsulfonic acid phosphinate copolymer at 35% solids, pH of 4.08 and number average molecular weight of 1468.

**[0073]** EXAMPLE 7

**[0074]** Into a round bottomed reaction flask equipped with two dropping funnels, reflux condenser, nitrogen inlet, temperature probe, and stirrer, there were charged 263.0 g vinylsulfonic acid solution (25%), 72.3g sodium allylsulfonate and 0.72g (0.0081 moles) sodium hypophosphite. While introducing nitrogen into the flask, the temperature was increased to 100°C. Then, 68.3 g of an aqueous solution of 55% acrylic acid and 181.3 g of a 17% sodium persulfate solution were added separately and simultaneously dropwise through separate dropping funnels over 5 hours. The addition rates of the two vessels were: persulfate solution at 36 ml/hr and acrylic acid at 13 ml/hr. After addition of the reactants was completed, the solution was aged for 1 hour at 80°C and then was left standing for cooling to room temperature. Once cooled, 50% sodium

hydroxide solution was added to provide a sodium salt of vinylsulfonic acid/maleic/acrylic acid/phosphinate terpolymer having 40% solids, pH of 4.02 and number average molecular weight of 1461.

**[0075]** Comparative Testing of the Polymers of Examples 1-7.

5 **[0076]** TABLE 1 shows some physical properties of the traceable polymeric scale inhibitors (Examples 1 – 7), commercially available polymers and the polymeric scale inhibitor without traceable moiety (Example 2). The number-average molecular weight (Mn) and polydispersity index (PDI) of the polymeric samples were determined using a gel permeation chromatography available from Waters having four aqueous columns set  
10 up in series: Waters ultrahydrogel one each of 500, 250 and two 120, and equipped with a differential refractive index detector, Waters 2414 RI. Each sample was diluted with mobile phase to a concentration of 0.1 mg/ml, and 1000ml of the solution was injected onto a GPC in 4.79M acetonitrile (pH of 11.0) at room temperature.

TABLE 1

15

| Example     | pH (10% in DI water) | % solids | Mn   | PDI  |
|-------------|----------------------|----------|------|------|
| 1           | 4.01                 | 40       | 1352 | 1.80 |
| 2           | 4.03                 | 47       | 1218 | 2.05 |
| 3           | 4.22                 | 43       | 1772 | 1.35 |
| 4           | 4.11                 | 44       | 369  | 2.41 |
| 5           | 3.97                 | 38       | 750  | 1.49 |
| 6           | 4.08                 | 35       | 1468 | 2.69 |
| 7           | 4.62                 | 40       | 1461 | 2.86 |
| Accent 1100 | 4.47                 | 47       | 1399 | 2.82 |
| Accent 1121 | 5.23                 | 38       | 6767 | 5.52 |
| PPCA        | 4.40                 | 49       | 1842 | 2.41 |

20

**[0077]** Determination of Minimum Inhibitor Concentration (MIC) in Calcium Carbonate

25

**[0078]** The brines stated in the NACE Standard TM0347-2007 (Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and/or Calcium Carbonate from Solution for Oil and Gas Production Systems), also known as “the static bottle or jar test,” was used to test the polymeric samples and determine their MIC in calcium carbonate.

[0079] All tests were performed at a temperature of 71°C, pH of 5.5 and 24 hour residence time. TABLE 2 shows the compositions of calcium carbonate brines used for all tests (in mg/L).

5

TABLE 2

| Ion       | NACE calcium carbonate brine |                 |
|-----------|------------------------------|-----------------|
|           | Calcium brine                | Carbonate brine |
| Sodium    | 12987                        | 14996           |
| Calcium   | 3306                         | 0               |
| Carbonate | 0                            | 5346            |
| Magnesium | 440                          | 0               |
| TDS*      | 16733                        | 20342           |

\*TDS = Total Dissolved Solids

[0080] The traceable scale inhibitors of Examples 1-7, and the commercially available scale inhibitors (Accent 1100, Accent 1121 and PPCA) were subjected to the NACE static bottle tests to determine their efficiencies in inhibiting the precipitation of calcium carbonate scale from the solution. The MIC was taken at the polymer concentration that gave a minimum of 80% inhibition efficiency.

[0081] The percentage inhibition was calculated using the following relationship:

$$\% inhibition = \left( \frac{C_a - C_b}{C_c - C_b} \right) \times 100$$

where  $C_a$  is the concentration of calcium ions ( $Ca^{2+}$ ) in the tested sample after precipitation,  $C_b$  is the concentration of calcium ions ( $Ca^{2+}$ ) in the blank after precipitation,  $C_c$  is the concentration of calcium ions ( $Ca^{2+}$ ) in the blank before precipitation.

[0082] TABLE 3 shows the comparative MIC's of the traceable scale inhibitor of Examples 1-7 and of the commercially available scale inhibitors (Accent 1100, Accent 1121 and PPCA) against calcium carbonate scales.

25

TABLE 3

| Example     | MIC for Calcium Carbonate* |
|-------------|----------------------------|
| 1           | 5-15 ppm                   |
| 2           | 15 ppm                     |
| 3           | >25 ppm                    |
| 4           | 15 ppm                     |
| 5           | 15-25 ppm                  |
| 6           | 15 ppm                     |
| 7           | 25 ppm                     |
| Accent 1100 | 5-15 ppm                   |
| Accent 1121 | 15-25 ppm                  |
| PPCA        | 5-15 ppm                   |

\* The test was performed at the concentration of scale inhibitor of 5, 15 and 25 ppm (all polymers tested had dry weight solids of 35.6%).

5

[0083] TABLE 3 shows that the traceable scale inhibitors of Example 1 exhibited a superior MIC for inhibiting the precipitation of calcium carbonate scale compared to the commercially available Accent 1121 and equal MIC to Accent 1100.

[0084] Determination of Scale Inhibition Efficiency against Barium Sulfate

10

[0085] Dynamic scale loop (DSL) or tube blocking test was used to determine the MIC of the traceable scale inhibitors of Examples 1-7 and the commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA against barium sulfate scale.

[0086] TABLE 4 shows the compositions of barium brine used for the DSL tests (in mg/L).

15

TABLE 4

| Ion       | Barium Brine | Sulfate Brine |
|-----------|--------------|---------------|
| Sodium    | 5392         | 5392          |
| Calcium   | 1250         | 0             |
| Sulfate   | 0            | 910           |
| Barium    | 376          | 0             |
| Magnesium | 63           | 0             |
| TDS*      | 7081         | 6302          |

\*TDS = Total Dissolved Solids

[0087] The tests for barium sulfate were performed at a temperature of 30°C and a pressure of 150 psi using an automatic dynamic scale loop system model PMAC DSL available from Process Measurement and Control (PMAC) Systems, Ltd equipped with an oven commercially available from Memmert GmbH & Co. KG. The test coil was a one meter stainless steel tube with an inner diameter of 1.0 mm. The flow rate through the test coil was 10 mL/min. A fail for barium sulfate scale was when a change in differential pressure across the test coil of 2 psi was observed.

[0088] Figure 1 shows the differential pressures across the test coil as a function of time. The DSL tests were performed for a blank sample (i.e., without any scale inhibitor), the commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA, and the traceable scale inhibitor of Examples 1-4.

[0089] As shown in Figure 1, the traceable scale inhibitor of Examples 1-7 are far superior in inhibiting the precipitation of barium sulfate scale than all three of the commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA.

[0090] Determination of Minimum Inhibitor Concentrations (MIC)

[0091] The minimum inhibitor concentration (MIC) of the traceable scale inhibitor of Examples 1-7 and the commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA were determined using the dynamic scale loop (DSL) test as described in the determination of scale inhibition efficiency against barium sulfate.

[0092] The traceable scale inhibitor of Examples 1-7 and commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA each were subjected to the DSL test. Scale rate was identified by measuring the change in pressure differential across the test coil over 40 minutes, two times the scaling time required for the blank (20 minutes). A maximum scale rate occurred when no inhibitor was added to the solution. The minimum inhibitor concentration (MIC) was defined as an amount of inhibitor required to keep the differential pressure from reaching 2 psi.

[0093] TABLE 5 shows the MIC concentrations of the traceable scale inhibitor of Examples 1-7 and the commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA.

TABLE 5

| Sample ID   | Minimum Inhibitor<br>Concentration MIC<br>(ppm) |
|-------------|-------------------------------------------------|
|             | Barite                                          |
| Example 1   | 10                                              |
| Example 2   | 10-20                                           |
| Example 3   | 20-40                                           |
| Example 4   | 10-20                                           |
| Example 5   | 10                                              |
| Example 6   | 10                                              |
| Example 7   | 20                                              |
| Accent 1100 | 20-40                                           |
| Accent 1121 | 20                                              |
| PPCA        | 40-60                                           |

**[0094]** The traceable scale inhibitors of Examples 1-7 all had significantly lower MIC's than the commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA under the harsh barite conditions. The barium sulfate scale occurred when the concentration of Examples 1-7 was less than 20 ppm, while the barium sulfate scale took place when the concentration of commercially available scale inhibitors Accent 1100, Accent 1121 and PPCA was less than 100, 80 and 60 ppm respectively.

**[0095]** Determination of Traceable Efficiency

**[0096]** The traceable efficiency of the traceable scale inhibitor 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.

**[0097]** The tested traceable scale inhibitor of known concentration was dissolved in 10 ml of water. To a 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 xylenol 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.

[0098] 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 complex with all phosphinate moiety present in the tested solution.

[0099] 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:

$$\text{Conc. of Traceable Scale Inhibitor} = [9.337 \times \text{ppm of Thorium Titrant added}] - 0.698$$

\*ppm of thorium titrant added is indicated on the graduated syringe, included with the test kit, at the end of the titration.

[0100] Therefore, the amount of traceable polymeric scale inhibitor in the tested solution (e.g., oilfield liquid) may be determined simply and quickly by visually titrating the tested solution using Palintest Organo-phosphonate test and then correlating the concentration of standard thorium solution at end point to the traceable scale inhibitor. The traceable phosphinate moiety in the tested solution is detectable to levels as low as 0.50 ppm based on a dried polymer weight using the Palintest Organophosphonate test described herein.

[0101] While the disclosure has been described by reference to various specific

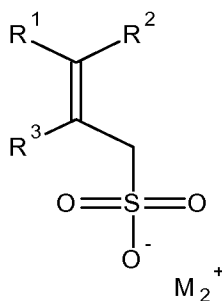
embodiments, it should be understood that numerous changes may be made within the spirit and scope of the inventive concepts described. Accordingly, it is intended that the invention not be limited to the described embodiments, but will have full scope defined by the language of the following claims.

## CLAIMS

1. A traceable polymeric scale inhibitor comprising a scale inhibiting moiety and a traceable phosphinate moiety, the scale inhibiting moiety comprising sulfonate functionality.
- 5 2. The traceable polymeric scale inhibitor of claim 1 derived from a mixture comprising:
  - a phosphinate compound selected from the group consisting of hypophosphite, inorganic phosphinate salts, organic phosphinate salts, and combinations thereof; and
  - a vinyl sulfonate-based monomer represented by structure (I):

10

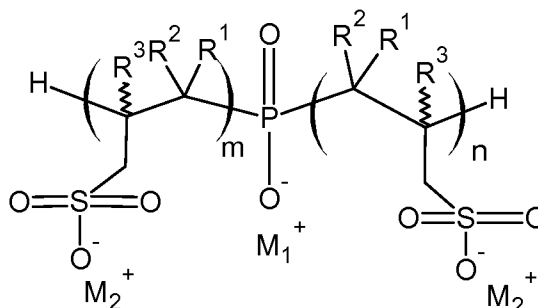
(I)



- wherein  $R^1$ ,  $R^2$  and  $R^3$  are independently hydrogen, an alkyl group having up to 7 carbon atoms, or a hydroxyl group; and  $M_2$  is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  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.

3. The traceable polymeric scale inhibitor of claim 2, wherein the vinyl sulfonate-based monomer includes a member selected from the group consisting of vinyl sulfonic acid, vinyl sulfonate, allylsulfonic acid, styrene sulfonic acid, sodium styrene sulfonate, allyloxy benzenesulfonic acid, 2-hydroxy-3-(2-propenyloxy)-propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, and salts thereof.
4. The traceable polymeric scale inhibitor of claim 1, comprising structure (III):

(III)



wherein

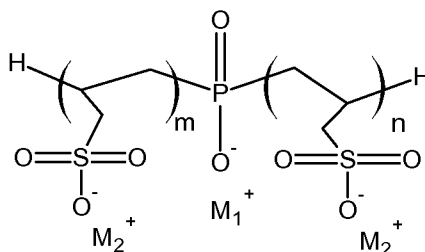
m and n are independently integral numbers;

5 a sum of m plus n is greater than 2; and

M<sub>1</sub> and M<sub>2</sub> are independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbon atoms.

10 **5.** The traceable polymeric scale inhibitor of claim 1, comprising structure (IV):

(IV)



15 wherein

m and n are independently integral numbers;

a sum of m plus n is greater than 2; and

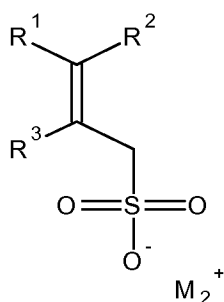
M<sub>1</sub> and M<sub>2</sub> are independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxy group having from 1 to 7 carbon atoms.

20 **6.** The traceable polymeric scale inhibitor of claim 1, wherein the scale inhibiting moiety comprising sulfonate functionality and carboxylate functionality.

7. The traceable polymeric scale inhibitor of claim 1, derived from a mixture comprising:

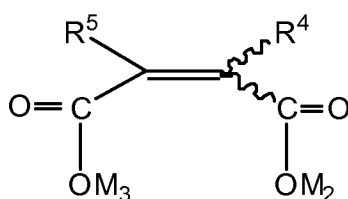
- a phosphinate compound selected from the group consisting of hypophosphite,  
 5 inorganic phosphinate salts, organic phosphinate salts, and combinations thereof;  
 a vinyl sulfonate-based monomer represented by structure (I):

(I)

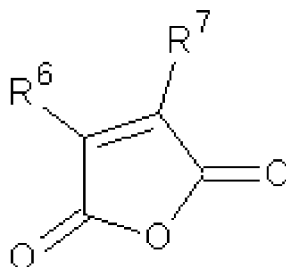


- 10 wherein  $R^1$ ,  $R^2$  and  $R^3$  are independently hydrogen, an alkyl group having up to 7 carbon atoms, or a hydroxyl group; and M is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbon atoms; and  
 15 a dicarboxylate monomer which includes a compound represented by structure (VII) or (VIII):

(VII)



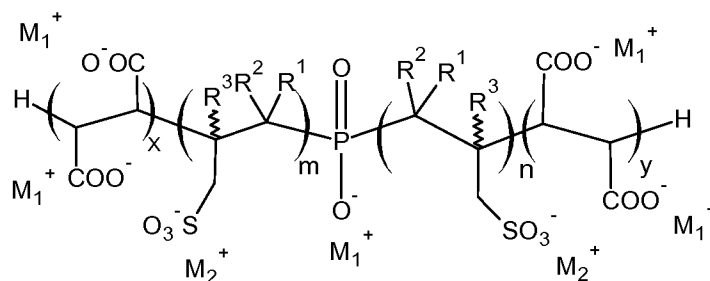
(VIII)



wherein  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are independently hydrogen, an alkyl group having up to 7 carbon atoms, or a hydroxyl group;  $M_2$  and  $M_3$  are independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  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 alkoxyl group having from 1 to 7 carbon atoms.

8. The traceable polymeric scale inhibitor of claim 7, wherein the dicarboxylate monomer includes a member selected from the group consisting of 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.

9. The traceable polymeric scale inhibitor of claim 1, comprising a structure:



where  $R^1$ ,  $R^2$ ,  $R^3$  are independently hydrogen, an alkyl group having up to 7 carbon atoms, a hydroxyl group, a carboxylate group or  $NR_1R_2$  where  $R_1$  and  $R_2$  are independently hydrogen, an alkyl group having from 1 to 7 carbon atoms, or an alkoxyl group having from 1 to 7 carbon atoms; and  $M_1$  and  $M_2$  each is independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium, and  $NR_1R_2R_3R_4$  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 alkoxyl group having from 1 to 7 carbon atoms.

10. The traceable polymeric scale inhibitor of claim 1, wherein an amount of the traceable phosphinate moiety is from about 0.01% to about 20.0% weight based on total weight of the polymeric scale inhibitor.

11. The traceable polymeric scale inhibitor of claim 1, wherein an amount of the traceable phosphinate moiety is from about 0.1% to about 2.0% weight based on total weight of the polymeric scale inhibitor.

12. The traceable polymeric scale inhibitor of claim 1, having a weight average molecular weight from about 1000 Daltons to about 15000 Daltons.

**13.** The traceable polymeric scale inhibitor of claim 1, having an effective minimum inhibition concentration (MIC) of less than about 50 ppm.

**14.** A method of reducing scale formation comprising:

treating fluid subjected to scale formation with a traceable polymeric scale inhibitor, wherein the traceable polymeric scale inhibitor comprises a scale inhibiting moiety and a traceable phosphinate moiety, the scale inhibiting moiety comprising sulfonate functionality.

**15.** The method of claim 14, wherein the scale inhibiting moiety comprises sulfonate functionality and carboxylate functionality.

10

**16.** The method of claim 14, wherein the fluid subjected to scale formation includes oilfield fluids.

**17.** The method of claim 14, comprising adding the traceable polymeric scale inhibitor periodically, continually or continuously to produced water or injection water.

**18.** The method of claim 14, comprising applying the traceable polymeric scale inhibitor to the subterranean formations by squeeze treatment.

**19.** The method of claim 14, further comprising:

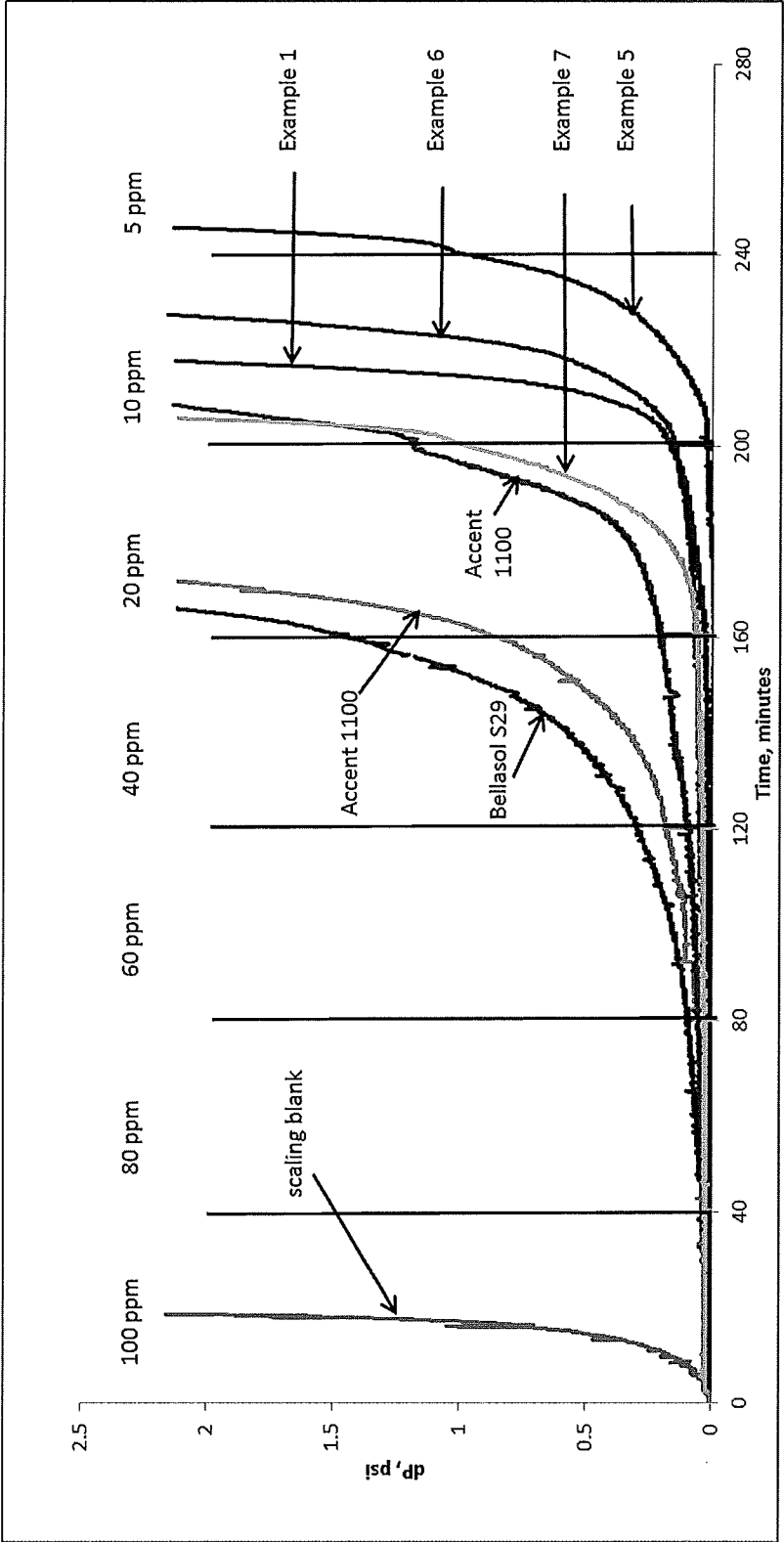
measuring an amount of the traceable polymeric scale inhibitor in the fluids periodically, continually or continuously; and

adding the traceable polymeric scale inhibitor to the fluids when the measured amount of traceable polymeric scale inhibitor is approaching a minimum inhibition concentration of the traceable polymeric scale inhibitor.

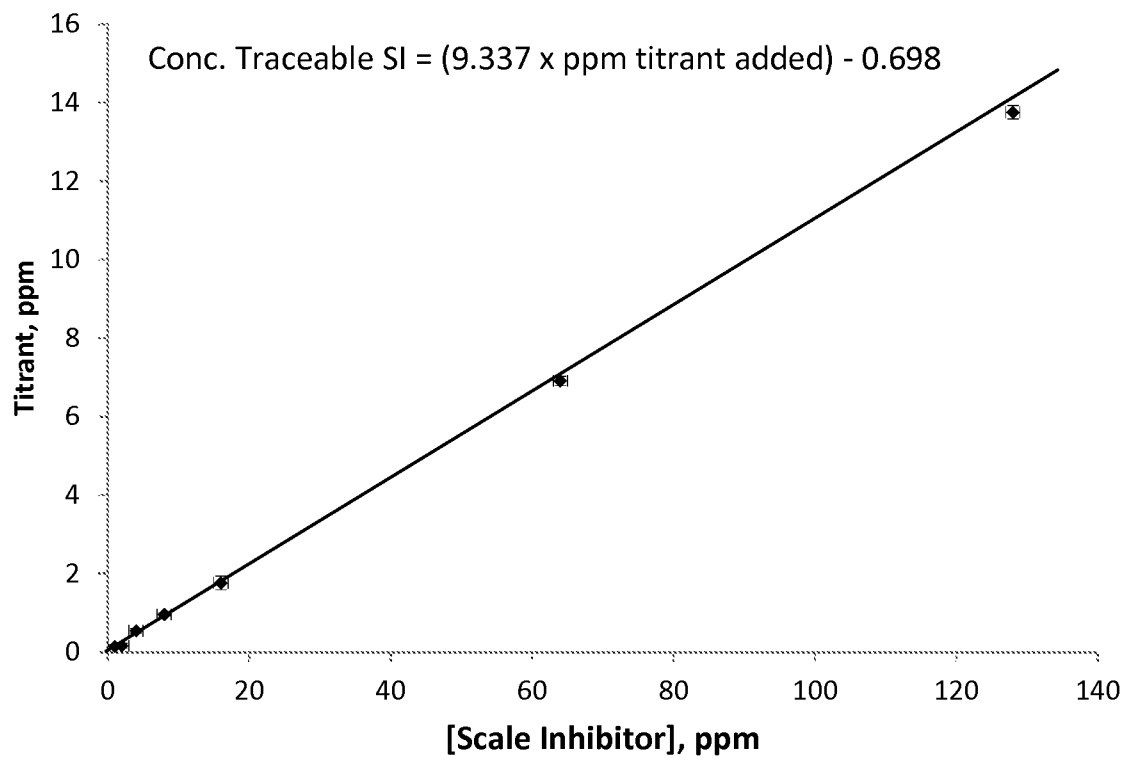
**20.** The method of claim 19, wherein measuring an amount of the traceable polymeric scale inhibitor in the fluids comprises titrating the traceable polymeric scale inhibitor with a color-forming agent.

**21.** The method of claim 14, wherein the fluid subjected to scale formation includes fluid in a system selected from the group consisting of cooling tower water systems; boiler water systems; hot water heaters; heat exchangers; mineral process waters; paper mill water systems; black liquor evaporators in the pulp industry; desalination systems; cleaning system; pipelines; gas scrubber systems; continuous casting processes in the metallurgical industry; air conditioning and refrigeration systems; industrial and petroleum process water; water reclamation and purification systems; membrane filtration water systems; food processing streams; and waste treatment systems.

FIG. 1



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FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2013/062138A. CLASSIFICATION OF SUBJECT MATTER  
INV. C02F5/14  
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)  
C02F

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages         | Relevant to claim No.      |
|-----------|--------------------------------------------------------------------------------------------|----------------------------|
| X<br>A    | US 2009/101587 A1 (BLOKKER PETER [NL] ET AL) 23 April 2009 (2009-04-23)<br>claims<br>----- | 1-3,6-8,<br>10-21<br>4,5,9 |



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

15 January 2014

Date of mailing of the international search report

04/02/2014

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/062138

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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