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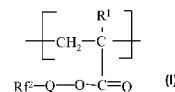
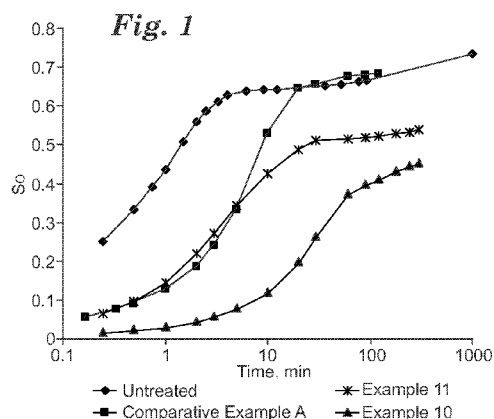
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[Continued on next page]

(54) Title: METHOD FOR TREATING HYDROCARBON-BEARING FORMATIONS WITH FLUOROALKYL SILANES



(57) Abstract: A method of treating a hydrocarbon-bearing formation, which includes contacting the hydrocarbon-bearing formation with a treatment composition, the treatment composition includes solvent and a fluorinated silane, wherein the fluorinated silane is selected from the group consisting of: a fluorinated silane represented by formula $\text{R}_1\text{-SO}_2\text{-N(R)}(\text{C}_n\text{H}_{2n})\text{-Si(Y)}_w(\text{Y})_{3-w}$; a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by (formula I) and at least one of a second divalent unit comprising a pendent $-\text{Si(Y)}_w(\text{Y})_{3-w}$ group; or a monovalent unit comprising a thioether linkage and at least one terminal $-\text{Si(Y)}_w(\text{Y})_{3-w}$ group; and combinations thereof. Hydrocarbon-bearing formations treated with fluorinated silanes or siloxanes are also disclosed.



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METHOD FOR TREATING HYDROCARBON-BEARING FORMATIONS WITH FLUOROALKYL SILANES

Cross Reference to Related Applications

This application claims the benefit of U. S. Provisional Application No. 61/185,645, filed June 10, 2009, the disclosure of which is incorporated by reference herein in its entirety.

Background

Fluorochemical compounds are commercially useful, for example, for surface-energy modification and may provide desirable macroscopic properties (e.g., soil repellency and soil release).

In the oil and gas industry, some hydrocarbon and fluorochemical compounds have been used to modify the wettability of reservoir rock, which may be useful, for example, to prevent or remedy water blocking (e.g., in oil or gas wells) or liquid hydrocarbon accumulation (e.g., in gas wells) in the vicinity of the wellbore (i.e., the near wellbore region). Water blocking and liquid hydrocarbon accumulation may result from natural phenomena (e.g., water-bearing geological zones or condensate banking) and/or operations conducted on the well (e.g., using aqueous or hydrocarbon fluids). Water blocking and condensate banking in the near wellbore region of a hydrocarbon-bearing geological formation can inhibit or stop production of hydrocarbons from the well and hence are typically not desirable. Not all hydrocarbon and fluorochemical compounds, however, provide the desired wettability modification. And some of these compounds modify the wettability of siliciclastic hydrocarbon-bearing formations but not carbonate formations, or vice versa. Hence, there is a continuing need for alternative and/or improved techniques for increasing the productivity of oil and/or gas wells that have brine and/or two phases of hydrocarbons in a near wellbore region of a hydrocarbon-bearing geological formation.

Summary

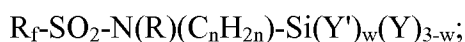
The methods of treating a hydrocarbon-bearing formation disclosed herein are typically useful for increasing the permeability in hydrocarbon-bearing formations having

at least one of brine (e.g., connate brine and/or water blocking) or two phases of hydrocarbons (i.e., an oil phase and a gas phase) in the near wellbore region. Treatment of an oil and/or gas well that has brine and/or two phases of hydrocarbons in the near wellbore region using the methods disclosed herein may increase the productivity of the well. Although not wishing to be bound by theory, it is believed that the fluorinated silanes disclosed herein generally at least one of adsorb to, chemisorb onto, or react with hydrocarbon-bearing formations under downhole conditions and modify the wetting properties of the rock in the formation to facilitate the removal of hydrocarbons and/or brine. Methods according to the present disclosure are useful for changing the wettability of a variety of materials found in hydrocarbon-bearing formations, including sand, sandstone, and calcium carbonate. Thus, the treatment methods are more versatile than other treatment methods which are effective with only certain substrates (e.g., sandstone). Methods disclosed herein can be carried out with one treatment step (i.e., application of one treatment composition). The fluorinated silanes useful for practicing the present disclosure can also be delivered to hydrocarbon-bearing formations at a variety of temperatures.

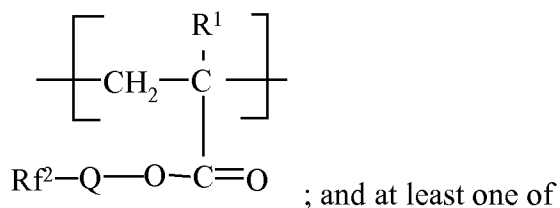
In one aspect, the present disclosure provides a method of treating a hydrocarbon-bearing formation, the method comprising:

contacting the hydrocarbon-bearing formation with a treatment composition, the treatment composition comprising solvent and a fluorinated silane, wherein the fluorinated silane is selected from the group consisting of:

(a) a fluorinated silane represented by formula



(b) a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by



(i) a second divalent unit comprising a pendent $-Si(Y')_w(Y)_{3-w}$ group;

or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ group; and

(c) combinations thereof;

wherein

R_f is fluoroalkyl having up to 6 carbon atoms;

each R_f^2 is independently fluoroalkyl having up to 6 carbon atoms;

each Q is independently selected from the group consisting of

$-\text{C}_m\text{H}_{2m}-$, $-\text{SO}_2\text{N}(\text{R})\text{C}_m\text{H}_{2m}-$, and $-\text{C}_y\text{H}_{2y}\text{SO}_2\text{N}(\text{R})\text{C}_y\text{H}_{2y}-$;

m and n are each independently in a range from 1 to 11;

each y is independently in a range from 1 to 6;

R is selected from the group consisting of hydrogen, alkyl having one to eight carbon atoms, and aryl;

each R^1 is independently hydrogen or methyl;

each Y is independently a hydrolyzable group;

each Y' is independently a non-hydrolyzable group; and

each w is independently 0, 1, or 2;

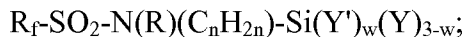
wherein the method does not include intentionally fracturing the hydrocarbon-bearing formation. In some embodiments, the fluorinated silane is represented by formula $\text{R}_f-\text{SO}_2-\text{N}(\text{R})(\text{C}_n\text{H}_{2n})-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$, wherein R_f is perfluorobutyl, R is alkyl having one to four carbon atoms, and n is an integer from 2 to 6. In other embodiments, the fluorinated silane is the nonionic compound (e.g., a nonionic polymer), wherein R_f^2 is perfluorobutyl, Q is $-\text{SO}_2-\text{N}(\text{R})-\text{C}_m\text{H}_{2m}-$, R is alkyl having one to four carbon atoms, and m is an integer from 2 to 6. In some embodiments, the method further comprises bonding the hydrocarbon-bearing formation with a fluorinated siloxane, wherein the fluorinated siloxane comprises at least one condensation product of the fluorinated silane. In some of these embodiments, the fluorinated siloxane shares at least one siloxane bond with the hydrocarbon-bearing formation.

In another aspect, the present disclosure provides a hydrocarbon-bearing formation treated according to the methods disclosed herein.

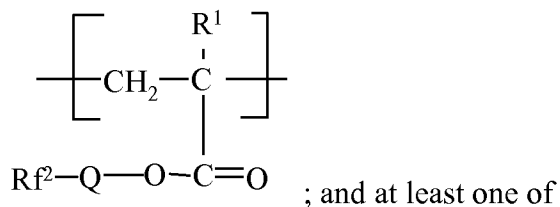
In another aspect, the present disclosure provides a composition comprising a hydrocarbon-bearing formation and a fluorinated compound bonded to the hydrocarbon-

bearing formation, wherein the fluorinated compound is selected from the group consisting of:

(a) a fluorinated silane represented by formula



(b) a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by



(i) a second divalent unit comprising a pendent $-Si(Y')_w(Y)_{3-w}$ group;

or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-Si(Y')_w(Y)_{3-w}$ group;

(c) combinations thereof; and

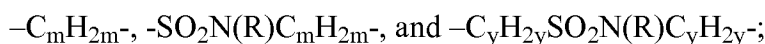
(d) condensation products thereof;

wherein

R_f is fluoroalkyl having up to 6 carbon atoms;

each Rf^2 is independently fluoroalkyl having up to 6 carbon atoms;

each Q is independently selected from the group consisting of



m and n are each independently in a range from 1 to 11;

each y is independently in a range from 1 to 6;

R is selected from the group consisting of hydrogen, alkyl having one to eight carbon atoms, and aryl;

each R^1 is independently hydrogen or methyl;

each Y is independently a hydrolyzable group;

each Y' is independently a non-hydrolyzable group; and

each w is independently 0, 1, or 2;

wherein the hydrocarbon-bearing formation is free of manmade fractures. In some embodiments, the fluorinated compound shares at least one siloxane bond with the

hydrocarbon-bearing formation. In some embodiments, the fluorinated compound is bonded (e.g., covalently bonded) to an inorganic component of the hydrocarbon-bearing formation. In some embodiments, the fluorinated compound is a condensation product of a fluorinated silane represented by formula $R_f-SO_2-N(R)(C_nH_{2n})-Si(Y)_w(Y)_{3-w}$, wherein R_f is perfluorobutyl.

In some embodiments of the foregoing aspects, the hydrocarbon-bearing formation is not in contact with proppants. In some embodiments, the hydrocarbon-bearing formation is an oil-bearing formation (e.g., a volatile oil well or black oil well).

To facilitate the understanding of this disclosure, a number of terms are defined below. Terms defined herein have meanings as commonly understood by a person of ordinary skill in the areas relevant to the present disclosure. Terms such as "a", "an", "at least one", and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terms "a", "an", and "the" are used interchangeably with the term "at least one".

The term "brine" refers to water having at least one dissolved electrolyte salt therein (e.g., having any nonzero concentration, and which may be less than 0.1 percent, or greater than 0.1 percent, greater than 1 percent, greater than 2 percent, 3 percent, 4 percent, 5 percent, 10 percent, 15 percent, or greater than 20 percent).

The term "hydrocarbon-bearing formation" includes both hydrocarbon-bearing formations in the field (i.e., subterranean hydrocarbon-bearing formations) and portions of such hydrocarbon-bearing formations (e.g., core samples).

The term "treating" includes placing a composition within a hydrocarbon-bearing formation using any suitable manner known in the art (e.g., pumping, injecting, pouring, releasing, displacing, spotting, or circulating the fluorinated polymer into a well, wellbore, or hydrocarbon-bearing formation).

The term "solvent" refers to a homogeneous liquid material, which may be a single compound or a combination of compounds and which may or may not include water, that is capable of at least partially dissolving the fluorinated silane at 25 °C.

"Alkyl group" and the prefix "alk-" are inclusive of both straight chain and branched chain groups and of cyclic groups. Unless otherwise specified, alkyl groups herein have up to 20 carbon atoms. Cyclic groups can be monocyclic or polycyclic and, in

some embodiments, have from 3 to 10 ring carbon atoms. "Alkylene" refers to the divalent form of the "alkyl" groups.

The term "aryl" as used herein includes carbocyclic aromatic rings or ring systems, for example, having 1, 2, or 3 rings and optionally containing at least one heteroatom (e.g., O, S, or N) in the ring. Examples of aryl groups include phenyl, naphthyl, biphenyl, fluorenyl as well as furyl, thienyl, pyridyl, quinoliny, isoquinoliny, indolyl, isoindolyl, triazolyl, pyrrolyl, tetrazolyl, imidazolyl, pyrazolyl, oxazolyl, and thiazolyl. "Arylene" is the divalent form of the "aryl" groups defined above.

"Arylalkylene" refers to an "alkylene" moiety to which an aryl group is attached.

The term "polymer" refers to a molecule having a structure which essentially includes the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass. The term "polymer" encompasses oligomers. Polymers may have repeating units from the same monomer or a combination of monomers.

The term "fluoroalkyl group" includes linear, branched, and/or cyclic alkyl groups in which all C-H bonds are replaced by C-F bonds (i.e., perfluoroalkyl groups) as well as groups in which hydrogen or chlorine atoms are present instead of fluorine atoms provided that up to one atom of either hydrogen or chlorine is present for every two carbon atoms. In some embodiments of fluoroalkyl groups, when at least one hydrogen or chlorine is present, the fluoroalkyl group includes at least one trifluoromethyl group. Unless otherwise specified, fluoroalkyl groups herein have up to 30 (e.g., up to 25, 20, 15, 12, 10, 8, or 6) fluorinated carbon atoms.

The term "productivity" as applied to a well refers to the capacity of a well to produce hydrocarbons (i.e., the ratio of the hydrocarbon flow rate to the pressure drop, where the pressure drop is the difference between the average reservoir pressure and the flowing bottom hole well pressure (i.e., flow per unit of driving force)).

The term "bonded" refers to having at least one of covalent bonding, hydrogen bonding, ionic bonding, Van Der Waals interactions, pi interactions, London forces, or electrostatic interactions.

The term "nonionic" refers to being free of ionic groups (e.g., salts) or groups (e.g., $-\text{CO}_2\text{H}$, $-\text{SO}_3\text{H}$, $-\text{OSO}_3\text{H}$, $-\text{P}(=\text{O})(\text{OH})_2$) that are readily ionized in water.

Fracturing a hydrocarbon-bearing formation refers to intentionally injecting a fluid into the hydrocarbon-bearing formation at a rate and pressure sufficient to open a fracture

therein. That is, the rate and pressure exceeds the rock strength. Typically, fracturing refers to hydraulic fracturing, and the fracturing fluid is a hydraulic fluid. Fracturing fluids may or may not contain proppants. Unintentional fracturing can sometimes occur, for example, during drilling of a wellbore. Unintentional fractures can be detected (e.g., by fluid loss from the wellbore) and repaired. Typically, fracturing a hydrocarbon-bearing formation refers to intentionally fracturing the formation after the wellbore is drilled. The term "free of manmade fractures" refers to the hydrocarbon-bearing formation being free of fractures made by this process.

The phrase "comprises at least one of" followed by a list refers to comprising any one of the items in the list and any combination of two or more items in the list. The phrase "at least one of" followed by a list refers to any one of the items in the list and any combination of two or more items in the list.

All numerical ranges are inclusive of their endpoints and non-integral values between the endpoints unless otherwise stated.

Brief Description of the Drawings

For a more complete understanding of the features and advantages of the present disclosure, reference is now made to the detailed description along with the accompanying figures and in which:

Fig. 1 is a graph showing a comparison of n-decane imbibition for Examples 10 and 11, Comparative Example A, and an untreated core;

Fig. 2 is a graph showing a comparison of n-decane imbibition for Examples 10 and 13 and an untreated core;

Fig. 3 is a graph showing a comparison of the pressure drop from an n-decane injection for Example 14, before and after treatment;

Fig. 4 is a graph showing a comparison of the pressure drop from an n-decane injection for Example 15, before and after treatment;

Fig. 5 is a graph showing a comparison of the pressure drop from an n-decane injection for Example 15, before and after treatment;

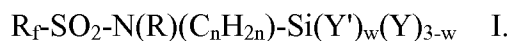
Fig. 6 is a schematic illustration of an exemplary embodiment of an offshore oil platform operating an apparatus for progressively treating a near wellbore region according to some embodiments of the present disclosure; and

Fig. 7 is a schematic illustration of the flow set-up used for Examples 1 to 9.

Fig. 8 is a schematic illustration of the core treatment set-up used for Examples 10 to 13 and the single phase oil injection evaluation set-up used for Examples 14 to 16.

Detailed Description

In some embodiments, fluorinated silanes useful for practicing the present disclosure are represented by the following formula (I):



R_f is fluoroalkyl having up to 6 carbon atoms (e.g., in a range from 1 to 6, 2 to 6, 3 to 6, or 3 to 4 carbon atoms). R_f can be a linear, branched, and/or cyclic structure. Representative R_f groups include trifluoromethyl, perfluoroethyl, 1,1,2,2-tetrafluoroethyl, 2-chlorotetrafluoroethyl, perfluoro-n-propyl, perfluoroisopropyl, perfluoro-n-butyl, 1,1,2,3,3,3-hexafluoropropyl, perfluoroisobutyl, perfluoro-*sec*-butyl, perfluoro-*tert*-butyl, perfluoro-n-pentyl, perfluoroisopentyl, or perfluorohexyl. In some embodiments, R_f is perfluorobutyl (e.g., perfluoro-n-butyl, perfluoroisobutyl, or perfluoro-*sec*-butyl). Suitable fluorinated silanes of formula I include a mixture of isomers (e.g., a mixture of compounds containing linear and branched perfluoroalkyl groups).

In formula I, R is hydrogen, alkyl having one to eight (e.g., 1 to 6, 1 to 4, or 1 to 2) carbon atoms, or aryl (e.g., phenyl). In some embodiments, R is alkyl having up to 4, 3, or 2 carbon atoms. In some embodiments, R is methyl.

In formula I, n is an integer from 1 to 11 (e.g., 2 to 11, 2 to 6, or 2 to 4). In some embodiments, n is 2 or 3. Groups represented by formula (C_nH_{2n}) include linear and branched structures.

Each Y in formula I is a hydrolysable group, which may be selected from the group consisting of halogen (i.e., -F, -Cl, -Br, or -I), alkoxy (e.g., having 1 to 6, 1 to 4, or 1 to 2 carbon atoms), aryloxy (e.g., phenoxy), acyloxy (e.g., having 1 to 6, 1 to 4, or 1 to 2 carbon atoms), and polyalkyleneoxy. "Polyalkyleneoxy" refers to $-O-(CHR^5-CH_2O)_q-R^3$ wherein R^3 is C_{1-4} alkyl, R^5 is hydrogen or methyl, with at least 70% of R^5 being hydrogen, and q is 1 to 40, or in some embodiments 2 to 10. In some embodiments, each Y is independently halogen (e.g., Cl or Br), alkoxy having one to six carbon atoms (e.g., having 1 to 4 or 1 to 2 carbon atoms), acyloxy having one to six carbon atoms (e.g., having 1 to 4 or 1 to 2 carbon atoms), or aryloxy (e.g., phenoxy). In some embodiments,

Y is methoxy or ethoxy. Hydrolysable groups Y are capable of hydrolyzing, for example, in the presence of water, optionally under acidic or basic conditions, producing groups capable of undergoing a condensation reaction, for example silanol groups.

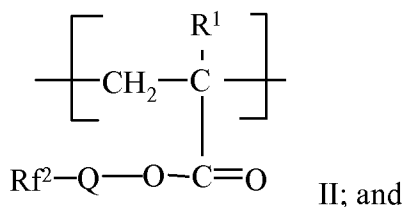
In formula I, Y' is a non-hydrolyzable group (i.e., a group that cannot be hydrolyzed in the presence of water). In some embodiments, Y' is independently alkyl having one to six carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl) or aryl having six to ten carbon atoms (e.g., phenyl). In some embodiments, Y' is alkyl having up to 4, 3, or 2 carbon atoms.

In formula I, w is 0, 1, or 2. In some embodiments, w is 0. In some embodiments, w is 1.

Methods of making fluorinated silanes of formula I are known in the art (e.g., by alkylation of fluorinated alcohols or sulfonamides with chloroalkyltrialkoxysilanes, or alkylation with allyl chloride followed by hydrosilation with HSiCl_3) (see, e.g., U.S. Pat. No. 5,274,159 (Pellerite et al.), the disclosure of which is incorporated herein by reference).

In some embodiments of the methods disclosed herein, the fluorinated silane is $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OR}')_3$ where each R' is independently selected from the group consisting of methyl and ethyl. In some embodiments, each R' is methyl. In some embodiments, each R' is ethyl.

In some embodiments, fluorinated silanes useful for practicing the present disclosure are nonionic compounds free of alkyleneoxy groups and comprising at least one first divalent unit represented by the following formula (II)



at least one of (i) a second divalent unit comprising a pendent $-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ group; or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ group. The phrase at least one of (i) or (ii) used herein means that the nonionic compound comprises (i) only, (ii) only, or both (i) and (ii). In some embodiments, the nonionic compound comprises both (i) and (ii).

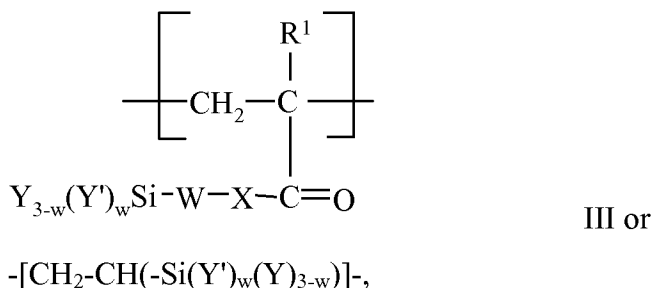
In formula II, each Rf^2 is independently fluoroalkyl group having up to 6 carbon atoms (e.g., in a range from 1 to 6, 2 to 6, 3 to 6, or 3 to 4 carbon atoms). Rf^2 can be a branched, linear, and/or cyclic structure. Exemplary Rf^2 groups include trifluoromethyl, perfluoroethyl, 1,1,2,2-tetrafluoroethyl, 2-chlorotetrafluoroethyl, perfluoro-n-propyl, perfluoroisopropyl, perfluoro-n-butyl, 1,1,2,3,3,3-hexafluoropropyl, perfluoroisobutyl, perfluoro-*sec*-butyl, perfluoro-*tert*-butyl, perfluoro-n-pentyl, perfluoroisopentyl, or perfluorohexyl). In some embodiments, Rf^2 is perfluorobutyl (e.g., perfluoro-n-butyl, perfluoroisobutyl, or perfluoro-*sec*-butyl). Useful fluoroalkyl groups include those having a mixture of structures and chain lengths (e.g., a mixture of linear and branched perfluoroalkyl groups).

In formula II, Q is $-C_mH_{2m}-$, $-SO_2N(R)C_mH_{2m}-$, or $-C_yH_{2y}SO_2N(R)C_yH_{2y}-$, wherein R is defined as above in any of the embodiments of R, m is an integer from 1 to 11 (e.g., 2 to 11, 2 to 6, or 2 to 4), and each y is independently an integer from 1 to 6 (in some embodiments from 2 to 4). In some embodiments, m is 2 or 3. In some embodiments, each y is independently 2 or 3. Groups represented by formula $-C_mH_{2m}-$ and $-C_yH_{2y}-$ include linear and branched structures.

In formula II, each R^1 is independently hydrogen or methyl. In some embodiments, R^1 is hydrogen. In some embodiments, R^1 is methyl.

In some embodiments, the number of units represented by formula II is in a range from 1 to 100 (in some embodiments from 1 to 20). In some embodiments, the units represented by formula II are present in a range from 40% by weight to 80% by weight (or from 50% to 75% by weight) based on the total weight of the nonionic compound. In some embodiments, the polymeric fluorinated composition contains at least 5 mole % (based on total moles of monomers) of Y groups. In some embodiments, the nonionic compound is a polymer having a weight average molecular weight in a range from 1,000 to 100,000, from 2,000 to 100,000, from 3,500 to 100,000, or from 10,000 to 75,000 grams per mole or in a range from 1,000 to 20,000, or from 2,000 to 10,000 grams per mole. Weight average molecular weights can be measure, for example, by gel permeation chromatography (i.e., size exclusion chromatography) using techniques known in the art. It will be appreciated by one skilled in the art that such polymers can exist as a mixture of compositions and molecular weights.

In some embodiments, the nonionic compound useful for practicing the present disclosure comprises a second divalent unit comprising a pendent $-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ group. In some of these embodiments, the second divalent unit is represented by the following formula (III):

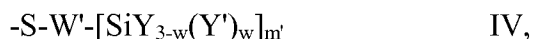


wherein, R^1 , Y, Y', and w are as defined above, each X is independently selected from the group consisting of $-\text{NH}-$, $-\text{O}-$, and $-\text{S}-$ (in some embodiments, $-\text{O}-$); and each W is independently selected from the group consisting of alkylene, arylalkylene, and arylene, wherein alkylene is optionally interrupted or substituted by at least one heteroatom (i.e., $-\text{NH}-$, $-\text{O}-$, or $-\text{S}-$). The term "interrupted" refers to groups in which there is an alkylene segment on each side of the heteroatom (e.g., $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$). In some embodiments, W is alkylene (e.g., having up to 6, 5, 4, or 3 carbon atoms). In some embodiments, the second divalent unit is represented by formula

$-\text{[CH}_2-\text{CH}(-\text{Si}(\text{Y}')_w(\text{Y})_{3-w})]-$, wherein Y, Y', and w are as defined above. A combination of second divalent units of formulas III and $-\text{[CH}_2-\text{CH}(-\text{Si}(\text{Y}')_w(\text{Y})_{3-w})]-$ may also be useful.

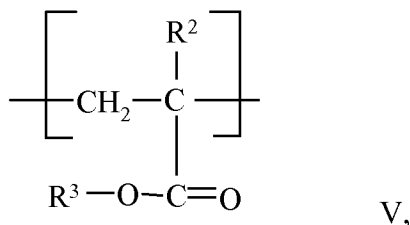
In some embodiments, the number of second divalent units represented by formula III or $-\text{[CH}_2-\text{CH}(-\text{Si}(\text{Y}')_w(\text{Y})_{3-w})]-$ is in a range from 0 to 100 (or even from 0 to 20). In the cases in which the number of second divalent units is 0, the nonionic compound contains at least one chain-terminating group represented by the following formula (IV). In some embodiments, the second divalent units are present in a range from 1% to 20% by weight (or even 2% to 15% by weight) based on the total weight of the nonionic compound.

In some embodiments, the nonionic compound comprises a monovalent unit comprising a thioether linkage and at least one terminal $-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ group, for example, a chain-terminating group represented by the following formula (IV):



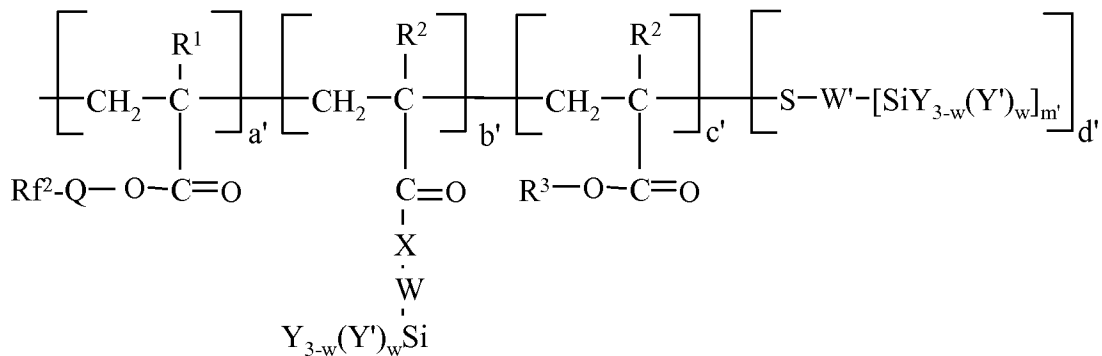
wherein Y, Y', and w are as defined above in any of their various embodiments, m' is 1 or 2, and W' is a divalent or trivalent linking group selected from the group consisting of alkylene, arylalkylene, and arylene, wherein alkylene is optionally interrupted by at least one ether linkage, ester linkage, carbamate, urea, or amide linkage. In some embodiments, W' is alkylene that is optionally interrupted by at least one carbamate, urea, amide, or ester linkage. In some embodiments, W' is ethylene or propylene. In some embodiments, W' is a divalent alkylene group, and m' is 1. In some embodiments, W' is a trivalent alkylene group, and m' is 2.

In some embodiments, the nonionic compound comprises at least one third divalent unit represented by the following formula (V):



wherein each R² is hydrogen or methyl; and each R³ is independently alkyl having from 1 to 30 (e.g., 1 to 25, 1 to 20, 3 to 25, 3 to 20, or 8 to 20) carbon atoms. In some embodiments, the number of third divalent units represented by formula V is in a range from 0 to 100 (or even from 0 to 20). In some embodiments, the third divalent units are present in a range from 1% to 20% by weight (or even 2% to 15% by weight) based on the total weight of the nonionic compound. Unexpectedly, nonionic compounds comprising up to 20% by weight of third divalent units effectively increase the permeability of sand and calcium carbonate to both liquid hydrocarbons and water.

In some embodiments, the nonionic compound is represented by formula



wherein R¹, Rf², Q, X, Y, Y', W', W, w, R³, and R² are as defined above; m' is 1 or 2; a' is a value from 1 to 100 inclusive; b' and c' are each independently values from 0 to 100

inclusive, and d' is a value from 0 to 1 inclusive, with the proviso that at least b' or d' is at least 1. Each of the units is independently in random order.

A divalent unit of formula II is typically introduced into a nonionic compound useful for practicing the present disclosure by reacting a monomer represented by formula $\text{CH}_2=\text{C}(\text{R}^1)-\text{C}(\text{O})-\text{O}-\text{Q}-\text{Rf}^2$, for example, under free-radical conditions. Fluorochemical monomers represented by this formula and methods for the preparation thereof are known in the art (see, e.g., U.S. Pat. No. 2,803,615 (Ahlbrecht et al.), the disclosure of which is incorporated herein by reference). Further examples of such compounds include acrylates or methacrylates derived from fluorochemical telomer alcohols, acrylates or methacrylates derived from fluorochemical carboxylic acids, and perfluoroalkyl acrylates or methacrylates as disclosed in U.S. Pat. No. 5,852,148 (Behr et al.), the disclosure of which is incorporated herein by reference.

Some useful monomers represented by formula $\text{CH}_2=\text{C}(\text{R}^1)-\text{C}(\text{O})-\text{O}-\text{Q}-\text{Rf}^2$ include $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, $\text{C}_5\text{F}_{11}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{C}_6\text{F}_{13}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, $\text{C}_3\text{F}_7\text{SO}_2\text{N}(\text{C}_4\text{H}_9)\text{C}_2\text{H}_4\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{C}_5\text{F}_{11}\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_3\text{S}(\text{O})_2\text{N}(\text{R}^a)-(\text{CH}_2)_2-\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_3\text{S}(\text{O})_2\text{N}(\text{R}^a)-(\text{CH}_2)_2-\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, and $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_{2-8}(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$, wherein R^a represents methyl, ethyl or n-butyl.

For embodiments in which the nonionic compound comprises a second divalent unit comprising a pendent $-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ group, a monomer represented by formula $\text{CH}_2=\text{C}(\text{R}^1)-\text{C}(\text{O})-\text{O}-\text{Q}-\text{Rf}^2$ can be reacted, for example, with a monomer represented by formula $\text{CH}_2=\text{C}(\text{R}^1)-\text{C}(\text{O})-\text{X}-\text{W}-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ or $\text{CH}_2=\text{C}(\text{R}^1)-\text{Si}(\text{Y}')_w(\text{Y})_{3-w}$ wherein R^1 , W, X, Y, Y', and w are as defined above in any of their various embodiments. Some monomers represented by these formulas are commercially available (e.g., $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ (available, for example, from Union Carbide, New York, NY, under the trade designation "A-174"), vinyltrichlorosilane,

vinyltrimethoxysilane, and vinyltriethoxysilane); others can be made by conventional synthetic methods.

For embodiments in which the nonionic compound comprises a third divalent unit represented by formula V, a monomer selected from alkyl acrylates and methacrylates (e.g., octadecyl methacrylate, lauryl methacrylate, butyl acrylate, isobutyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, methyl methacrylate, hexyl acrylate, heptyl methacrylate, cyclohexyl methacrylate, or isobornyl acrylate) can be added to the reaction mixture comprising the monomer represented by formula $\text{CH}_2=\text{C}(\text{R}^1)-\text{C}(\text{O})-\text{O}-\text{Q}-\text{Rf}^2$.

Nonionic compounds useful for practicing the present disclosure may contain other units, typically in weight percents up to 20, 15, 10, or 5 percent, based on the total weight of the nonionic compound. These units may be incorporated into the compound by selecting additional components for the free-radical reaction such as allyl esters (e.g., allyl acetate and allyl heptanoate); vinyl ethers or allyl ethers (e.g., cetyl vinyl ether, dodecylvinyl ether, 2-chloroethylvinyl ether, or ethylvinyl ether); alpha-beta unsaturated nitriles (e.g., acrylonitrile, methacrylonitrile, 2-chloroacrylonitrile, 2-cyanoethyl acrylate, or alkyl cyanoacrylates); alpha-beta-unsaturated carboxylic acid derivatives (e.g., allyl alcohol, allyl glycolate, acrylamide, methacrylamide, n-diisopropyl acrylamide, or diacetoneacrylamide), styrene and its derivatives (e.g., vinyltoluene, alpha-methylstyrene, or alpha-cyanomethyl styrene); olefinic hydrocarbons which may contain at least one halogen (e.g., ethylene, propylene, isobutene, 3-chloro-1-isobutene, butadiene, isoprene, chloro and dichlorobutadiene, 2,5-dimethyl-1,5-hexadiene, and vinyl and vinylidene chloride); and hydroxyalkyl-substituted polymerizable compounds (e.g., 2-hydroxyethyl methacrylate). In some embodiments, the nonionic compounds are free of anionic groups (e.g., carboxylates, sulfates, sulfonates, phosphates, and phosphonates). In some embodiments, the nonionic compounds are free of cationic groups (e.g., quaternary amine groups), and in other embodiments, the nonionic compounds are free of poly(alkyleneoxy) groups. In some embodiments, the nonionic compounds are free of anionic groups, cationic groups, and poly(alkyleneoxy) groups. Unexpectedly, nonionic compounds that are free of such water-solubilizing groups effectively change the permeability of sand and calcium carbonate to water and liquid hydrocarbons.

Nonionic compounds useful for practicing the present invention may have a chain-terminating group represented by formula IV. A chain-terminating group of formula IV

may be incorporated into the nonionic compound, for example, by adding a chain-transfer agent of the formula $\text{HS-W}'\text{-}[\text{SiY}_{3-w}(\text{Y}')_w]_{m'}$ to the reaction mixture comprising the monomer represented by formula $\text{CH}_2=\text{C}(\text{R}^1)\text{-C}(\text{O})\text{-O-Q-Rf}^2$. For the chain-transfer agent represented by formula $\text{HS-W}'\text{-}[\text{SiY}_{3-w}(\text{Y}')_w]_{m'}$ the groups W' , Y , Y' , m' , and w may have any definition described above for monovalent units represented by formula IV. Some chain-transfer agents of formula $\text{HS-W}'\text{-}[\text{SiY}_{3-w}(\text{Y}')_w]_{m'}$ are commercially available (e.g., 3-mercaptopropyltrimethoxysilane (available, for example, from Huls America, Inc., Somerset, N.J., under the trade designation "DYNASYLAN")); others can be made by conventional synthetic methods. A chain-terminating group of formula IV can also be incorporated into a nonionic compound as disclosed herein by including in the free-radical reaction mixture a hydroxyl-functional chain-transfer agent (e.g., 2-mercaptoethanol, 3-mercapto-2-butanol, 3-mercapto-2-propanol, 3-mercapto-1-propanol, 3-mercapto-1,2-propanediol) and subsequent reaction of the hydroxyl functional group with, for example, a chloroalkyltrialkoxysilane. In a reaction mixture to make a nonionic compound disclosed herein, a single chain transfer agent or a mixture of different chain transfer agents may be used to obtain the desired molecular weight of the nonionic compound.

The nonionic compound useful for practicing the present disclosure can conveniently be prepared through a free radical reaction of a fluorinated monomer with optionally a non-fluorinated monomer (e.g., an alkyl acrylate or methacrylate) and at least one of a monomer containing a silyl group or a chain transfer agent containing a silyl group using methods known in the art. Free radical initiators such as those widely known and used in the art may be used to initiate reaction of the components. Examples of free-radical initiators include azo compounds (e.g., 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis(2-methylbutyronitrile), or azo-2-cyanovaleric acid); hydroperoxides (e.g., cumene, *tert*-butyl or *tert*-amyl hydroperoxide); dialkyl peroxides (e.g., di-*tert*-butyl or dicumylperoxide); peroxyesters (e.g., *tert*-butyl perbenzoate or di-*tert*-butyl peroxyphthalate); diacylperoxides (e.g., benzoyl peroxide or lauryl peroxide). Useful photoinitiators include benzoin ethers (e.g., benzoin methyl ether or benzoin butyl ether); acetophenone derivatives (e.g., 2,2-dimethoxy-2-phenylacetophenone or 2,2-diethoxyacetophenone); and acylphosphine oxide derivatives and acylphosphonate derivatives (e.g., diphenyl-2,4,6-trimethylbenzoylphosphine oxide, isopropoxyphenyl-2,4,6-trimethylbenzoylphosphine oxide, or dimethyl pivaloylphosphonate). When heated

or photolyzed such free-radical initiators fragment to generate free radicals which add to ethylenically unsaturated bonds and initiate free-radical reactions.

Free-radical reactions may be carried out in any suitable solvent at any suitable concentration, (e.g., from about 5 percent to about 90 percent by weight based on the total weight of the reaction mixture). Examples of suitable solvents include aliphatic and alicyclic hydrocarbons (e.g., hexane, heptane, cyclohexane), aromatic solvents (e.g., benzene, toluene, xylene), ethers (e.g., diethyl ether, glyme, diglyme, diisopropyl ether), esters (e.g., ethyl acetate, butyl acetate), alcohols (e.g., ethanol, isopropyl alcohol), ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone), sulfoxides (e.g., dimethyl sulfoxide), amides (e.g., N,N-dimethylformamide, N,N-dimethylacetamide), halogenated solvents (e.g., methylchloroform, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloroethylene or trifluorotoluene), and mixtures thereof.

While it is not practical to enumerate a particular temperature suitable for all initiators and all solvents, generally suitable temperatures are in a range from about 30 °C to about 200 °C. Particular temperature and solvents for use can be selected by those skilled in the art based on considerations such as the solubility of reagents, the temperature required for the use of a particular initiator, and the molecular weight desired.

Typical chain transfer agents (in addition to or instead of those described above) that may be used in the preparation of nonionic compounds herein include hydroxyl-substituted mercaptans (e.g., 2-mercaptoethanol, 3-mercapto-2-butanol, 3-mercapto-2-propanol, 3-mercapto-1-propanol, and 3-mercapto-1,2-propanediol (i.e., thioglycerol)); amino-substituted mercaptans (e.g., 2-mercaptoethylamine); difunctional mercaptans (e.g., di(2-mercaptoethyl)sulfide); and aliphatic mercaptans (e.g., octylmercaptan, dodecylmercaptan, and octadecylmercaptan).

Adjusting, for example, the concentration and activity of the initiator, the concentration of each of the reactive monomers, the temperature, the concentration of the chain transfer agent, and the solvent using techniques known in the art can control the molecular weight of a polyacrylate copolymer.

Typically, in treatment compositions useful for practicing the methods disclosed herein, the fluorinated silane is present in the treatment composition at at least 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.055, 0.06, 0.065, 0.07, 0.075, 0.08, 0.085, 0.09, 0.095, 0.1, 0.15, 0.2, 0.25, 0.5, 1, 1.5, 2, 3, 4, or 5 percent by weight, up to 5, 6, 7, 8,

9, 10, 15, 20, 25, or 30 percent by weight, based on the total weight of the composition. For example, the amount of the fluorinated silane in the treatment composition may be in a range of from 0.01 to 15, 0.1 to 10, 0.1 to 5, 1 to 10, or even in a range from 1 to 5 percent by weight, based on the total weight of the composition. Lower and higher amounts of the fluorinated silane in the treatment composition may also be used, and may be desirable for some applications.

Treatment compositions useful in practicing the present disclosure comprise solvent. Examples of useful solvents for any of these methods include organic solvents, water, easily gasified fluids (e.g., ammonia, low molecular weight hydrocarbons, and supercritical or liquid carbon dioxide), and combinations thereof. In some embodiments, the organic solvent is water-miscible. Examples of organic solvents useful for practicing the methods disclosed herein include polar solvents such as alcohols (e.g., methanol, ethanol, isopropanol, propanol, or butanol), glycols (e.g., ethylene glycol or propylene glycol), glycol ethers (e.g., ethylene glycol monobutyl ether or those glycol ethers available under the trade designation "DOWANOL" from Dow Chemical Co., Midland, MI), ketones (e.g., acetone, methyl ethyl ketone, 4-methyl-2-pentanone, 3-methyl-2-pentanone, 2-methyl-3-pentanone, and 3,3-dimethyl-2-butanone), esters (e.g., ethyl acetate, methyl formate, propyl acetate, and butyl acetate); ethers (e.g., diethyl ether, tetrahydrofuran (THF), diisopropyl ether, p-dioxane, *tert*-butyl methyl ether, and dipropyleneglycol monomethylether (DPM)); nitriles (e.g., acetonitrile); and formamides (e.g., dimethylformamide). The solvent (e.g., solvent mixture) may be selected so that it is capable of dissolving one or more fluorinated silanes disclosed herein and optionally any hydrolysis catalyst included in the treatment composition.

In some embodiments, the solvent comprises at least one of an alcohol, a ketone, a nitrile, a formamide, or a hydrocarbon. In some of these embodiments, the solvent comprises at least one of methanol, ethanol, propanol, butanol, acetone, acetonitrile, or dimethylformamide. In some embodiments, the solvent comprises at least one of kerosene, diesel, gasoline, pentane, hexane, heptane, mineral oil, or a naphthene. In some embodiments, the solvent is selected such that it has the formula Y-H where Y is the hydrolyzable group of the fluorinated silane. In some embodiments of the methods disclosed herein, the solvent comprises up to 95, 80, 75, 50, 40, 30, 20, or 10 percent by

weight of a monohydroxy alcohol having up to 4 carbon atoms, based on the total weight of the treatment composition.

In some embodiments, treatment compositions useful in practicing the present disclosure contain two or more different solvents. In some embodiments, the compositions comprise at least one of a polyol or polyol ether independently having from 2 to 25 (in some embodiments, 2 to 15, 2 to 10, 2 to 9, or even 2 to 8) carbon atoms and at least one of water, a monohydroxy alcohol, an ether, or a ketone, wherein the monohydroxy alcohol, the ether, and the ketone each independently have up to 4 carbon atoms. In some of these embodiments, the polyol or polyol ether is present in the composition at at least 50, 55, 60, or 65 percent by weight and up to 75, 80, 85, or 90 percent by weight, based on the total weight of the composition. The term "polyol" refers to an organic molecule consisting of C, H, and O atoms connected one to another by C-H, C-C, C-O, O-H single bonds, and having at least two C-O-H groups. In some embodiments, useful polyols (e.g., diols or glycols) have 2 to 25, 2 to 20, 2 to 15, 2 to 10, 2 to 8, or even 2 to 6 carbon atoms. In some embodiments, the solvent comprises a polyol ether. The term "polyol ether" refers to an organic molecule consisting of C, H, and O atoms connected one to another by C-H, C-C, C-O, O-H single bonds, and which is at least theoretically derivable by at least partial etherification of a polyol. In some embodiments, the polyol ether has at least one C-O-H group and at least one C-O-C linkage. Useful polyol ethers (e.g., glycol ethers) may have from 3 to 25 carbon atoms, 3 to 20, 3 to 15, 3 to 10, 3 to 9, 3 to 8, or even from 5 to 8 carbon atoms. In some embodiments, the polyol is at least one of ethylene glycol, propylene glycol, poly(propylene glycol), 1,3-propanediol, or 1,8-octanediol, and the polyol ether is at least one of 2-butoxyethanol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, or 1-methoxy-2-propanol. In some embodiments, the polyol and/or polyol ether has a normal boiling point of less than 450 °F (232 °C), which may be useful, for example, to facilitate removal of the polyol and/or polyol ether from a well after treatment. In these embodiments, in the event that a component of the solvent is a member of two functional classes, it may be used as either class but not both. For example, ethylene glycol methyl ether may be a polyol ether or a monohydroxy alcohol, but not as both simultaneously. In these embodiments, each solvent component may be present as a single component or a mixture of components.

Useful combinations of two solvents include 1,3-propanediol (80%)/isopropanol (IPA) (20%), propylene glycol (70%)/IPA (30%), propylene glycol (90%)/IPA (10%), propylene glycol (80%)/IPA (20%), ethylene glycol (50%)/ethanol (50%), ethylene glycol (70%)/ethanol (30%), propylene glycol monobutyl ether (PGBE) (50%)/ethanol (50%), PGBE (70%)/ethanol (30%), dipropylene glycol monomethyl ether (DPGME) (50%)/ethanol (50%), DPGME (70%)/ethanol (30%), diethylene glycol monomethyl ether (DEGME) (70%)/ethanol (30%), triethylene glycol monomethyl ether (TEGME) (50%)/ethanol (50%), TEGME (70%)/ethanol (30%), 1,8-octanediol (50%)/ethanol (50%), propylene glycol (70%)/tetrahydrofuran (THF) (30%), propylene glycol (70%)/acetone (30%), propylene glycol (70%), methanol (30%), propylene glycol (60%)/IPA (40%), 2-butoxyethanol (80%)/ethanol (20%), 2-butoxyethanol (70%)/ethanol (30%), 2-butoxyethanol (60%)/ethanol (40%), propylene glycol (70%)/ethanol (30%), ethylene glycol (70%)/IPA (30%), and glycerol (70%)/IPA (30%), wherein the exemplary percentages are by weight are based on the total weight of solvent.

In some embodiments of treatment compositions disclosed herein, the solvent comprises a ketone, ether, or ester having from 4 to 10 (e.g., 5 to 10, 6 to 10, 6 to 8, or 6) carbon atoms or a hydrofluoroether or hydrofluorocarbon. In some of these embodiments, the solvent comprises two different ketones, each having 4 to 10 carbon atoms (e.g., any combination of 2-butanone, 4-methyl-2-pentanone, 3-methyl-2-pentanone, 2-methyl-3-pentanone, and 3,3-dimethyl-2-butanone). In some embodiments, the solvent further comprises at least one of water or a monohydroxy alcohol having up to 4 carbon atoms (e.g., methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, isobutanol, and t-butanol). Useful ethers having 4 to 10 carbon atoms include diethyl ether, diisopropyl ether, tetrahydrofuran, p-dioxane, and *tert*-butyl methyl ether. Useful esters having 4 to 10 carbon atoms include ethyl acetate, propyl acetate, and butyl acetate. Useful hydrofluoroethers may be represented by the general formula $Rf^3-[O-R_h]_a$, wherein *a* is an integer from 1 to 3; Rf^3 is a perfluoroalkyl or di- or trivalent perfluoroalkylene, each of which may be interrupted with at least one -O-; and R_h is an alkyl group optionally interrupted with at least one -O-. Numerous hydrofluoroethers of this type are disclosed in U. S. Pat. No. 6,380,149 (Flynn et al.), the disclosure of which is incorporated herein by reference. In some embodiments, the hydrofluoroether is methyl perfluorobutyl ether or ethyl perfluorobutyl ether. Useful hydrofluoroethers also include hydrofluoroethers

available, for example, from 3M Company, St. Paul, MN, under the trade designations "HFE-7100" and "HFE-7200".

The amount of solvent typically varies inversely with the amount of other components in compositions according to and/or useful in practicing the present disclosure. For example, based on the total weight of the composition, the solvent may be present in the composition in an amount of from at least 50, 60, or 75 percent by weight or more up to 60, 70, 80, 90, 95, 98, or 99 percent by weight, or more.

In some embodiments, the solvent comprises water, for example, in an amount effective to hydrolyze the hydrolyzable groups. In some embodiments, the amount of water will be in a range from 0.1 to 30% by weight of the total treatment composition, in some embodiments up to 15% by weight, up to 10% by weight, or up to 5% by weight. In other embodiments, water is present in an amount of at least 1% by weight, at least 5% by weight, or at least 10% by weight of the total treatment composition.

In some embodiments, treatment compositions useful for practicing the present disclosure comprise one of an acidic compound or an alkaline compound strong enough to catalyze hydrolysis of a Si-Y bond. Useful acidic compounds include both organic and inorganic acids. Organic acids include acetic acid, citric acid, formic acid, trifluoromethanesulfonic (i.e., triflic) acid, perfluorobutyric acid, and combinations thereof. Inorganic acids include sulfuric acid, hydrochloric acid, hydroboric acid, phosphoric acid, and combinations thereof. The acid compounds also include acid precursors that form an acid when contacted with water. Combinations of any of these acids may also be useful. Useful alkaline compounds include amines, alkali metal hydroxides, alkaline earth metal hydroxides, and combinations thereof. Exemplary alkaline compounds include sodium hydroxide, potassium hydroxide, sodium fluoride, potassium fluoride, and trimethylamine.

Acidic or alkaline compounds strong enough to catalyze hydrolysis of the Si-Y bond can generally be used in amounts in a range from 0.01 to 10%, but may be used in amount of at least 0.05%, at least 0.1%, at least 1%, or at least 5%, and in amounts up to 8%, up to 5%, up to 1%, or up to 0.1%, by weight based on the total weight of the treatment composition.

The ingredients for treatment compositions described herein including fluorinated silanes, solvents, and optionally water and/or a hydrolysis catalyst can be combined using

techniques known in the art for combining these types of materials, including using conventional magnetic stir bars or mechanical mixer (e.g., in-line static mixer and recirculating pump).

In some embodiments, the methods disclosed herein are useful for hydrocarbon-bearing formations having brine. The brine present in the hydrocarbon-bearing formation may be from a variety of sources including at least one of connate water, flowing water, mobile water, immobile water, residual water from a fracturing operation or from other downhole fluids, or crossflow water (e.g., water from adjacent perforated formations or adjacent layers in the formations). The brine may cause water blocking in the hydrocarbon-bearing formation. Salts that may be present in the brine include sodium chloride, calcium chloride, strontium chloride, magnesium chloride, potassium chloride, ferric chloride, ferrous chloride, and hydrates thereof. It is believed that useful treatment compositions will not undergo precipitation of the fluorinated silanes, dissolved salts, or other solids when the treatment compositions encounter the brine. Such precipitation may inhibit the adsorption or reaction of the fluorinated silane on the formation, may clog the pores in the hydrocarbon-bearing formation thereby decreasing the permeability and the hydrocarbon and/or brine production, or a combination thereof.

In some embodiments, methods according to the present disclosure include receiving (e.g., obtaining or measuring) data comprising the temperature and the brine composition (including the brine saturation level and components of the brine) of a selected hydrocarbon-bearing formation. These data can be obtained or measured using techniques well known to one skilled in the art. In some embodiments, the methods comprise selecting a treatment composition for the hydrocarbon-bearing formation comprising the fluorinated silane and solvent, based on the behavior of a mixture of the brine composition and the treatment composition. Typically, for the methods disclosed herein, a mixture of an amount of brine and the treatment composition is transparent and substantially free of precipitated solid (e.g., salts, asphaltenes, or fluorinated silanes). Although not wanting to be bound by theory, it is believed the effectiveness of the methods disclosed herein for improving hydrocarbon productivity of a particular oil and/or gas well having brine accumulated in the near wellbore region will typically be determined by the ability of the composition to dissolve the quantity of brine present in the near wellbore region of the well while delivering the polymer to the well. Hence, at a

given temperature greater amounts of compositions having lower brine solubility (i.e., compositions that can dissolve a relatively lower amount of brine) will typically be required to treat a hydrocarbon-bearing formation than compositions having higher brine solubility but containing the same fluorinated silane at the same concentration.

As used herein, the term transparent refers to allowing clear view of objects beyond. In some embodiments, transparent refers to liquids that are not hazy or cloudy. The term "substantially free of precipitated solid" refers to an amount of precipitated solid that does not interfere with the ability of the fluorinated silane to increase the gas or liquid permeability of the hydrocarbon-bearing formation. In some embodiments, "substantially free of precipitated solid" means that no precipitated solid is visually observed. In some embodiments, "substantially free of precipitated solid" is an amount of solid that is less than 5% by weight higher than the solubility product at a given temperature and pressure.

In some embodiments, the transparent mixture of the brine composition and the treatment composition separates into at least two separate transparent liquid layers, and in other embodiments, the transparent mixture does not separate into layers. Phase behavior of a mixture of the brine composition and the treatment composition can be evaluated prior to treating the hydrocarbon-bearing formation by obtaining a sample of the brine from the hydrocarbon-bearing formation and/or analyzing the composition of the brine from the hydrocarbon-bearing formation and preparing an equivalent brine having the same or similar composition to the composition of the brine in the formation. The brine composition and the treatment composition can be combined (e.g., in a container) at the temperature and then mixed together (e.g., by shaking or stirring). The mixture is then maintained at the temperature for a certain time period (e.g., 15 minutes), removed from the heat, and immediately visually evaluated to see if phase separation, cloudiness, or precipitation occurs. The amount of the brine composition in the mixture may be in a range from 5 to 95 percent by weight (e.g., at least 10, 20, 30, percent by weight and up to 35, 40, 45, 50, 55, 60, or 70 percent by weight) based on the total weight of the mixture.

The phase behavior of the composition and the brine can be evaluated over an extended period of time (e.g., 1 hour, 12 hours, 24 hours, or longer) to determine if any phase separation, precipitation, or cloudiness is observed. By adjusting the relative amounts of brine (e.g., equivalent brine) and the treatment composition, it is possible to determine the maximum brine uptake capacity (above which precipitation occurs) of the

treatment composition at a given temperature. Varying the temperature at which the above procedure is carried out typically results in a more complete understanding of the suitability of treatment compositions for a given well.

In addition to using a phase behavior evaluation, it is also contemplated that one may be able to obtain the compatibility information, in whole or in part, by computer simulation or by referring to previously determined, collected, and/or tabulated information (e.g., in a handbook, table, or a computer database). In some embodiments, the selecting a treatment composition comprises consulting a table of compatibility data between brines and treatment compositions at different temperatures.

Whether the mixture of the brine composition and the treatment composition is transparent, substantially free of precipitated solid, and separates into layers at the temperature of the hydrocarbon-bearing formation can depend on many variables (e.g., concentration of the fluorinated silane, solvent composition, brine concentration and composition, hydrocarbon concentration and composition, and the presence of other components (e.g., surfactants or scale inhibitors)). Typically, for treatment compositions comprising at least one of a polyol or polyol ether described above and a monohydroxy alcohol having up to 4 carbon atoms, mixtures of the brine composition and the treatment composition do not separate into two or more layers. In some of these embodiments, the salinity of the brine is less than 15 percent (e.g., less than 14, 13, 12, or 11 percent) total dissolved salts. Typically, for treatment compositions described above comprising at least one (e.g., one or two) ketone having from 4 to 10 carbon atoms or a hydrofluoroether, mixtures of the brine composition and the treatment composition separate into two or more layers. In some of these embodiments, the salinity of the brine is greater than 10 percent (e.g., greater than 11, 12.5, 13, or 15 percent) total dissolved salt. Although not wishing to be bound by theory, it is believed that when two or more layers form in such mixtures, the fluorinated silane preferentially partitions into a layer rich in organic solvent that has a lower concentration of dissolved salts. Typically, treatment compositions comprising at least one of a polyol or polyol ether described above and treatment compositions comprising at least one ketone having from 4 to 10 carbon atoms or a hydrofluoroether are capable of solubilizing more brine (i.e., no salt precipitation occurs) in the presence of a fluorinated silane than methanol, ethanol, propanol, butanol, or acetone alone.

In some embodiments, the treatment composition further comprises a scale inhibitor. Useful scale inhibitors include polyacrylic acid, ethylenediaminetetraacetic acid, hydrochloric acid, formic acid, citric acid, acetic acid, phosphonates, phosphonic acids (e.g., 2-phosphono-, 1,2,4-butanetricarboxylic acid, amino(trimethylene) phosphonic acid), diposphonic acid, and phosphate esters. In some embodiments, the scale inhibitor is polyacrylic acid.

Typically the method disclosed herein modifies the wettability of the hydrocarbon-bearing formation. Wettability modification may help increase well deliverability of oil and/or gas in a hydrocarbon-bearing formation. Wettability can play a role in liquid accumulation around a wellbore. The effect of wettability on condensate accumulation in porous media can be expressed with the Young-Laplace equation: $P_c = (2\sigma\cos\theta)/r$ where the capillary pressure P_c is proportional to interfacial tension (σ) and the cosine of the pseudocontact angle ($\cos\theta$), and is inversely proportional to pore size (r). Thus, according to the Young-Laplace equation, decreasing the cosine of the pseudocontact angle for a given liquid will correspondingly decrease the capillary pressure and thus may increase well deliverability by decreasing, for example, condensate accumulation or water around a wellbore. In some embodiments, modifying the wettability of the hydrocarbon-bearing formation is selected from the group consisting of modifying the gas wetting, modifying the liquid wetting, and modifying a combination thereof. In some embodiments, the gas wetting is increased while the liquid wetting is decreased.

Reducing the rate of imbibition of materials such as water, oil, or both, may also improve well deliverability. Typically, the method disclosed herein reduces the rate of imbibition of oil in the hydrocarbon-bearing formation. One convenient proxy for measuring the rate of imbibition of hydrocarbon is the measurement of the rate of imbibition of n-decane on a core sample of the formation. Accordingly, in some embodiments, the method disclosed herein may further comprise reducing the rate of n-decane imbibition of the hydrocarbon-bearing formation. In other embodiments, the method may further comprise reducing the rate of water imbibition of the hydrocarbon-bearing formation.

In some embodiments, the method of treating a hydrocarbon-bearing formation disclosed herein reduces a rate of n-decane imbibition of the hydrocarbon-bearing to a greater extent than contacting an equivalent hydrocarbon-bearing formation with a

comparative composition, wherein the comparative composition is the same as the treatment composition except that the fluorinated silane is replaced with a fluorinated silane represented by formula $[C_4F_9SO_2N(CH_3)CH_2]_2CHOC(O)NH(CH_2)_3Si(OCH_2CH_3)_3$. For example, unexpectedly, a treatment composition comprising $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OCH_3)_3$ both reduces the rate of n-decane imbibition of a sandstone sample and provides a lower level of imbibition to the sandstone sample than a comparative composition comprising $[C_4F_9SO_2N(CH_3)CH_2]_2CHOC(O)NH(CH_2)_3Si(OCH_2CH_3)_3$, even though the number of fluorinated carbons is higher in the comparative composition; (see, e.g., the Examples below). The term "equivalent hydrocarbon-bearing formation" refers to a hydrocarbon-bearing formation that is similar to or the same (e.g., in chemical make-up, surface chemistry, brine composition, and hydrocarbon composition) as a hydrocarbon-bearing formation disclosed herein before it is treated with a method according to the present disclosure. In some embodiments, both the hydrocarbon-bearing formation and the equivalent hydrocarbon-bearing formation are siliciclastic formations, in some embodiments, greater than 50 percent sandstone. In some embodiments, the hydrocarbon-bearing formation and the equivalent hydrocarbon-bearing formation may have the same or similar pore volume and porosity (e.g., within 15 percent, 10 percent, 8 percent, 6 percent, or even within 5 percent).

In some embodiments of the treatment methods disclosed herein, the hydrocarbon-bearing formation has both liquid hydrocarbons and gas, and the hydrocarbon-bearing formation has at least a gas permeability that is increased after the hydrocarbon-bearing formation is treated with the treatment composition. In some embodiments, the gas permeability after treating the hydrocarbon-bearing formation with the composition is increased by at least 5 percent (in some embodiments, by at least 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, or 100 percent or more) relative to the gas permeability of the formation before treating the formation with the composition. In some embodiments, the gas permeability is a gas relative permeability. In some embodiments, the liquid (e.g., oil or condensate) permeability in the hydrocarbon-bearing formation is also increased (in some embodiments, by at least 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, or 100 percent or more) after treating the formation with the treatment composition.

To measure the effects of the method disclosed herein, it may be convenient to inject a liquid (e.g., oil, water, or condensate) into a core (e.g., a sandstone core or a limestone core) or a particulate pack (e.g., a sand pack or particulate calcium carbonate). This injection will produce a maximum pressure drop across the sandstone formation. When the wettability of the core, for example, is reduced for the liquid injected into the core, the effectiveness of the treatment may be manifested as a lower measured pressure drop. The pressure drop, if any, can be 5% or more with respect to the pressure across an untreated core, 10% or more, 20% or more, 30% or more, or 50% or more. The maximum pressure drop can be up to 95%, up to 90%, up to 75%, up to 70%, up to 50%, or up to 40%. Permeability can be calculated from the maximum pressure drop.

The hydrocarbon-bearing formation that can be treated according to the methods disclosed herein may have both gas and liquid hydrocarbons and may have gas condensate, black oil, or volatile oil. The hydrocarbons may comprise, for example, at least one of methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, decane, or higher hydrocarbons. The term "black oil" refers to the class of crude oil typically having gas-oil ratios (GOR) less than about 2000 scf/stb ($356 \text{ m}^3/\text{m}^3$). For example, a black oil may have a GOR in a range from about 100 (18), 200 (36), 300 (53), 400 (71), or even 500 scf/stb ($89 \text{ m}^3/\text{m}^3$) up to about 1800 (320), 1900 (338), or 2000 scf/stb ($356 \text{ m}^3/\text{m}^3$). The term "volatile oil" refers to the class of crude oil typically having a GOR in a range between about 2000 and 3300 scf/stb (356 and $588 \text{ m}^3/\text{m}^3$). For example, a volatile oil may have a GOR in a range from about 2000 (356), 2100 (374), or 2200 scf/stb ($392 \text{ m}^3/\text{m}^3$) up to about 3100 (552), 3200 (570), or 3300 scf/stb ($588 \text{ m}^3/\text{m}^3$). In some embodiments, the at least one of solvent or water (in the composition) at least partially solubilizes or at least partially displaces the liquid hydrocarbons in the hydrocarbon-bearing formation.

Generally, for the treatment methods disclosed herein, the amounts of the fluorinated silane and solvent (and type of solvent) is dependent on the particular application since conditions typically vary between wells, at different depths of individual wells, and even over time at a given location in an individual well. Advantageously, treatment methods according to the present disclosure can be customized for individual wells and conditions.

The hydrocarbon-bearing formations that may be treated according to the present disclosure may be siliciclastic (e.g., shale, conglomerate, diatomite, sand, and sandstone) or carbonate (e.g., limestone or dolomite) formations. In some embodiments, the hydrocarbon-bearing formation is predominantly sandstone (i.e., at least 50 percent by weight sandstone). In some embodiments, the hydrocarbon-bearing formation is predominantly limestone (i.e., at least 50 percent by weight limestone). The methods disclosed herein are unexpectedly effective at treating both sandstone and limestone hydrocarbon-bearing formations. In previous work, nonionic polymeric fluorinated surfactants have been shown to have limited effectiveness on limestone; (see, e.g., Comparative Example A in Int. Pat. Appl. Pub. No. WO 2009/148831 (Sharma et al.), the disclosure of which example is incorporated herein by reference).

Methods according to the present disclosure may be practiced, for example, in a laboratory environment (e.g., on a core sample (i.e., a portion) of a hydrocarbon-bearing formation or in the field (e.g., on a subterranean hydrocarbon-bearing formation situated downhole). Typically, the methods disclosed herein are applicable to downhole conditions having a pressure in a range from about 1 bar (100 kPa) to about 1000 bars (100 MPa) and have a temperature in a range from about 100 °F (38 °C) to 400 °F (204 °C) although the methods are not limited to hydrocarbon-bearing formations having these conditions. In some embodiments, the hydrocarbon-bearing formation that is treated has a temperature of up to 200 °F (93 °C), 175 °F (79 °C), 150 °F (66 °C), 125 °F (52 °C), or 100 °F (38 °C). Those skilled in the art, after reviewing the instant disclosure, will recognize that various factors may be taken into account in practice of the any of the disclosed methods including the ionic strength of the brine, pH (e.g., a range from a pH of about 4 to about 10), and the radial stress at the wellbore (e.g., about 1 bar (100 kPa) to about 1000 bars (100 MPa)).

In the field, treating a hydrocarbon-bearing formation with a composition described herein can be carried out using methods (e.g., by pumping under pressure) well known to those skilled in the oil and gas art. Coil tubing, for example, may be used to deliver the treatment composition to a particular geological zone of a hydrocarbon-bearing formation. In some embodiments of practicing the methods described herein it may be desirable to isolate a geological zone (e.g., with conventional packers) to be treated with the composition.

Methods described herein are useful, for example on both existing and new wells. Typically, it is believed to be desirable to allow for a shut-in time after treatment compositions described herein contact hydrocarbon-bearing formations. Exemplary shut-in times include a few hours (e.g., 1 to 12 hours), about 24 hours, or even a few (e.g., 2 to 10) days. After the treatment composition has been allowed to remain in place for a selected time, the solvents present in the composition may be recovered from the formation by simply pumping fluids up tubing in a well as is commonly done to produce fluids from a formation.

In some embodiments of treatment methods according to the present disclosure, the method comprises treating the hydrocarbon-bearing formation with a fluid prior to treating the hydrocarbon-bearing formation with the composition. In some embodiments, the fluid at least one of at least partially solubilizes or at least partially displaces brine or hydrocarbons in the hydrocarbon-bearing formation. In some embodiments, the fluid at least partially solubilizes brine. In some embodiments, the fluid at least partially displaces brine. In some embodiments, the fluid at least one of at least partially solubilizes or displaces liquid hydrocarbons in the hydrocarbon-bearing formation. In some embodiments, the fluid is substantially free of fluorochemicals. The term “substantially free of fluorochemicals” refers to fluid that may have a fluorochemical in an amount insufficient for the fluid to have a cloud point (e.g., when it is below its critical micelle concentration). A fluid that is substantially free of fluorochemical may be a fluid that has a fluorochemical but in an amount insufficient to alter the wettability of, for example, a hydrocarbon-bearing formation under downhole conditions. A fluid that is substantially free of fluorochemicals includes those that have a weight percent of such fluorochemicals as low as 0 weight percent. The fluid may be useful for decreasing the concentration of at least one of the salts present in a brine prior to introducing the composition to the hydrocarbon-bearing formation. The change in brine composition may change the results of a phase behavior evaluation (e.g., the combination of a composition with a first brine prior to the fluid preflush may result in salt precipitation while the combination of the treatment composition with the brine after the fluid preflush may result in a transparent mixture with no salt precipitation.)

In some embodiments of treatment methods disclosed herein, the fluid comprises at least one of toluene, diesel, heptane, octane, or condensate. In some embodiments, the

fluid comprises at least one of water, methanol, ethanol, or isopropanol. In some embodiments, the fluid comprises any of the solvents or solvent combinations mentioned above. In some embodiments, the fluid comprises at least one of nitrogen, carbon dioxide, or methane. In some embodiments, the fluid comprises a scale inhibitor (e.g., any of the scale inhibitors described above).

Advantageously, treatment methods disclosed herein typically provide an increase in at least one of the gas permeability, the hydrocarbon liquid permeability, or the water permeability of the formation without fracturing the formation. In the field, for example, manmade fractures are typically made by injecting a fracturing fluid into a subterranean geological formation at a rate and pressure sufficient to open a fracture therein (i.e., exceeding the rock strength). In some embodiments, hydrocarbon-bearing formations that may be treated according to the methods disclosed herein (e.g., limestone or carbonate formations) have natural fractures. Natural fractures may be formed, for example, as part of a network of fractures.

Referring to Fig. 6, an exemplary offshore oil platform is schematically illustrated and generally designated 10. Semi-submersible platform 12 is centered over submerged hydrocarbon-bearing formation 14 located below sea floor 16. Subsea conduit 18 extends from deck 20 of platform 12 to wellhead installation 22 including blowout preventers 24. Platform 12 is shown with hoisting apparatus 26 and derrick 28 for raising and lowering pipe strings such as work string 30.

Wellbore 32 extends through the various earth strata including hydrocarbon-bearing formation 14. Casing 34 is cemented within wellbore 32 by cement 36. Work string 30 may include various tools including, for example, sand control screen assembly 38 which is positioned within wellbore 32 adjacent to hydrocarbon-bearing formation 14. Also extending from platform 12 through wellbore 32 is fluid delivery tube 40 having fluid or gas discharge section 42 positioned adjacent to hydrocarbon-bearing formation 14, shown with production zone 48 between packers 44, 46. When it is desired to treat the near-wellbore region (a region within about 25 (in some embodiments, 20, 15, or 10) feet of the wellbore) of hydrocarbon-bearing formation 14 adjacent to production zone 48, work string 30 and fluid delivery tube 40 are lowered through casing 34 until sand control screen assembly 38 and fluid discharge section 42 are positioned adjacent to the near-wellbore region of hydrocarbon-bearing formation 14 including perforations 50.

Thereafter, a composition described herein is pumped down delivery tube 40 to progressively treat the near-wellbore region of hydrocarbon-bearing formation 14.

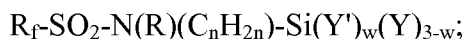
While the drawing depicts an offshore operation, the skilled artisan will recognize that the methods for treating a production zone of a wellbore are equally well-suited for use in onshore operations. Also, while the drawing depicts a vertical well, the skilled artisan will also recognize that methods according to the present disclosure are equally well-suited for use in deviated wells, inclined wells or horizontal wells.

Selected Embodiments of the Disclosure

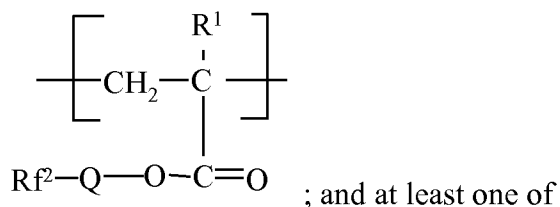
In a first embodiment, the present disclosure provides a method of treating a hydrocarbon-bearing formation, the method comprising:

contacting the hydrocarbon-bearing formation with a treatment composition, the treatment composition comprising solvent and a fluorinated silane, wherein the fluorinated silane is selected from the group consisting of:

(a) a fluorinated silane represented by formula



(b) a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by



(i) a second divalent unit comprising a pendent $-Si(Y')_w(Y)_{3-w}$ group;

or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-Si(Y')_w(Y)_{3-w}$ group; and

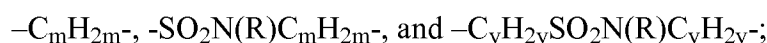
(c) combinations thereof;

wherein

R_f is fluoroalkyl having up to 6 carbon atoms;

each R_f^2 is independently fluoroalkyl having up to 6 carbon atoms;

each Q is independently selected from the group consisting of



m and n are each independently in a range from 1 to 11;

each y is independently in a range from 1 to 6;

R is selected from the group consisting of hydrogen, alkyl having one to eight carbon atoms, and aryl;

each R¹ is independently hydrogen or methyl;

each Y is independently a hydrolyzable group;

each Y' is independently a non-hydrolyzable group; and

each w is independently 0, 1, or 2;

wherein the method does not include intentionally fracturing the hydrocarbon-bearing formation.

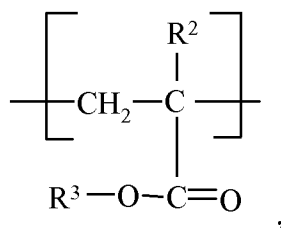
In a second embodiment, the present disclosure provides the method of embodiment 1, wherein each Y is independently selected from the group consisting of halogen, alkoxy having one to six carbon atoms, acyloxy having one to six carbon atoms, and aryloxy, and wherein each Y' is independently selected from the group consisting of alkyl having one to six carbon atoms and aryl having six to ten carbon atoms.

In a third embodiment, the present disclosure provides the method of embodiment 1 or 2, wherein R_f is perfluorobutyl, R is alkyl having one to four carbon atoms, and n is an integer from 2 to 6.

In a fourth embodiment, the present disclosure provides the method of any one of embodiments 1 to 3, wherein the fluorinated silane is C₄F₉SO₂N(CH₃)(CH₂)₃Si(OR')₃, wherein each R' is independently selected from the group consisting of methyl and ethyl.

In a fifth embodiment, the present disclosure provides the method of embodiment 1 or 2, wherein R^{f2} is perfluorobutyl, Q is -SO₂-N(R)-C_mH_{2m}-, wherein R is alkyl having one to four carbon atoms, and m is an integer from 2 to 6.

In a sixth embodiment, the present disclosure provides the method of embodiment 5, wherein the nonionic compound further comprises at least one third divalent unit represented by formula:



wherein

each R^2 is independently selected from the group consisting of hydrogen and methyl; and

each R^3 is independently alkyl having from 1 to 30 carbon atoms.

In a seventh embodiment, the present disclosure provides the method of any one of embodiments 1 to 6, wherein the solvent comprises water.

In an eighth embodiment, the present disclosure provides the method of any one of embodiments 1 to 7, wherein the solvent comprises at least one of an alcohol, ketone, glycol, glycol ether, hydrofluoroether, or hydrocarbon.

In a ninth embodiment, the present disclosure provides the method of any one of embodiments 1 to 8, wherein the solvent comprises at least one of methanol, ethanol, propanol, butanol, 2-butoxyethanol, or propylene glycol.

In a tenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 9, wherein the solvent comprises at least one of kerosene, diesel, gasoline, pentane, hexane, heptane, mineral oil, or a naphthene.

In an eleventh embodiment, the present disclosure provides the method of any one of embodiments 1 to 10, wherein the solvent comprises a ketone having from 4 to 10 carbon atoms or a hydrofluoroether.

In a twelfth embodiment, the present disclosure provides the method of any one of embodiments 1 to 11, further comprising:

receiving data comprising a temperature and a brine composition of the hydrocarbon-bearing formation; and

selecting a treatment composition for the hydrocarbon-bearing formation comprising the fluorinated silane and the solvent, wherein, at the temperature, a mixture of the brine composition and the treatment composition separates into at least two separate transparent liquid layers, and wherein the mixture is free of precipitated solid.

In a thirteenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 12, wherein the treatment composition further comprises an acidic compound selected from the group consisting of acetic acid, citric acid, formic acid, trifluoromethanesulfonic acid, perfluorobutyric acid, hydroboric acid, sulfuric acid, phosphoric acid, hydrochloric acid, and combinations thereof.

In a fourteenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 12, wherein the treatment composition further comprises an alkaline compound selected from the group consisting of an amine, an alkali metal hydroxide, an alkaline earth metal hydroxide, and combinations thereof.

In a fifteenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 14, wherein the hydrocarbon-bearing formation comprises at least one of sandstone, shale, conglomerate, diatomite, or sand.

In a sixteenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 14, wherein the hydrocarbon-bearing formation comprises at least one of carbonate or limestone.

In a seventeenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 16, wherein the hydrocarbon-bearing formation is downhole, the method further comprising obtaining at least one of oil or gas from the hydrocarbon-bearing formation.

In an eighteenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 17, wherein the hydrocarbon-bearing formation is an oil-bearing formation.

In a nineteenth embodiment, the present disclosure provides the method of any one of embodiments 1 to 18, further comprising contacting the hydrocarbon-bearing formation with a fluid before contacting the hydrocarbon-bearing formation with the composition, wherein the fluid at least one of at least partially solubilizes or partially displaces at least one of brine or liquid hydrocarbons in the hydrocarbon-bearing formation.

In a twentieth embodiment, the present disclosure provides the method of any one of embodiments 1 to 19, further comprising bonding the hydrocarbon-bearing formation with a fluorinated siloxane, wherein the fluorinated siloxane comprises at least one condensation product of the fluorinated silane.

In a twenty-first embodiment, the present disclosure provides the method of any one of embodiments 1 to 20, wherein the fluorinated siloxane shares at least one siloxane bond with the hydrocarbon-bearing formation.

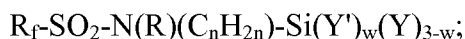
In a twenty-second embodiment, the present disclosure provides the method of any one of embodiments 1 to 21, wherein contacting the hydrocarbon-bearing formation with the treatment composition reduces a rate of n-decane imbibition of the hydrocarbon-

bearing to a greater extent than contacting an equivalent hydrocarbon-bearing formation with a comparative composition, wherein the comparative composition is the same as the treatment composition except that the fluorinated silane is replaced with a fluorinated silane represented by formula $[C_4F_9SO_2N(CH_3)CH_2]_2CHOC(O)NH(CH_2)_3Si(OCH_2CH_3)_3$.

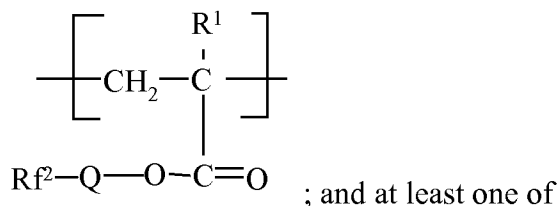
In a twenty-third embodiment, the present disclosure provides the method of any one of embodiments 1 to 22, wherein the hydrocarbon-bearing formation is at least one of not in contact with proppants or free of manmade fractures.

In a twenty-fourth embodiment, the present disclosure provides a composition comprising a hydrocarbon-bearing formation and a fluorinated compound bonded to the hydrocarbon-bearing formation, wherein the fluorinated compound is selected from the group consisting of:

(a) a fluorinated silane represented by formula



(b) a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by



(i) a second divalent unit comprising a pendent $-Si(Y')_w(Y)_{3-w}$ group;

or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-Si(Y')_w(Y)_{3-w}$ group;

(c) combinations thereof; and

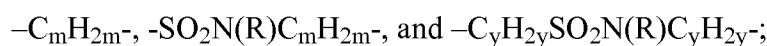
(d) condensation products thereof;

wherein

R_f is fluoroalkyl having up to 6 carbon atoms;

each Rf^2 is independently fluoroalkyl having up to 6 carbon atoms;

each Q is independently selected from the group consisting of



m and n are each independently in a range from 1 to 11;

each y is independently in a range from 1 to 6;

R is selected from the group consisting of hydrogen, alkyl having one to eight carbon atoms, and aryl;

each R¹ is independently hydrogen or methyl;

each Y is independently a hydrolyzable group;

each Y' is independently a non-hydrolyzable group; and

each w is independently 0, 1, or 2;

wherein the hydrocarbon-bearing formation is free of manmade fractures.

In a twenty-fifth embodiment, the present disclosure provides the composition of embodiment 24, wherein the fluorinated compound shares at least one siloxane bond with the hydrocarbon-bearing formation.

In a twenty-sixth embodiment, the present disclosure provides the composition of embodiment 24 or 25, wherein R_f is perfluorobutyl.

In a twenty-seventh embodiment, the present disclosure provides the composition of any one of embodiments 24 to 26, wherein the fluorinated compound is bonded to an inorganic component of the hydrocarbon-bearing formation.

Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure. Unless otherwise noted, all parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight. In the Tables, "nd" means not determined.

EXAMPLES

Preparation of 3-(N-Methylperfluorobutanesulfonamidopropyl)trimethoxysilane (C₄F₉SO₂N(CH₃)(CH₂)₃Si(OCH₃)₃):

For Examples 10-16, the following preparation was used. A mixture of about 626 grams (2 mol) of C₄F₉SO₂N(CH₃)H, generally made as described in U.S. Pat. No. 6,664,354 (Savu et al.), Example 1, Part A, the disclosure of which is incorporated herein by reference, about 432 grams (2 mol) of a 25% by weight NaOMe in MeOH, and 100 mL of diglyme was stripped on a rotovapor to leave a soft solid.

The resulting solid was transferred to a 3 liter, 3-neck paddle-stirred flask with about 400 mL of diglyme. The contents of the flask were stirred at 50°C. About 400 grams (2 mol) of $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ was added to the flask in a slow stream. The mixture was heated overnight at about 90 °C. Gas Chromatography showed incomplete reaction. The contents of the flask were then heated to about 120 °C for about 10 hours. Gas Chromatography showed the reaction was essentially complete. The resulting slurry was cooled to about 25 °C, and the NaCl filtered out. The resulting cake was rinsed with methylene chloride. The mixture was one-plate distilled to yield first diglyme at about 30 °C/1 mmHg (133 Pa) and then product at about 100-120 °C/0.3 mmHg (40 Pa).

For Examples 1, 3, 4, 6, and 8, the reaction was carried out on a 0.1 mole scale in 30 grams dry dimethylformamide. The $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{H}$ and NaOMe in methanol were heated at 50 °C for 1 hour under nitrogen before the methanol was removed under aspirator vacuum. The reaction mixture was cooled to 25 °C before $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ was added, and the resulting mixture was heated at 90 °C for 16 hours under nitrogen when analysis by Gas Chromatography indicated the reaction was complete.

Preparation of

MeFBSEA/ODMA/ $\text{CH}(\text{CH}_3)=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3/\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ at the molar ratio of (6:1:1:1) in isopropyl alcohol (Copolymer 1).

Part A

N-Methylperfluorobutanesulfonamidoethyl acrylate (N-MeFBSEA) was prepared according to the method of U.S. Pat. No. 6,664,354 (Savu), Example 2, Parts A and B, the disclosure of which is incorporated herein by reference, except using 4270 kilograms (kg) of N-methylperfluorobutanesulfonamidoethanol, 1.6 kg of phenothiazine, 2.7 kg of methoxyhydroquinone, 1590 kg of heptane, 1030 kg of acrylic acid, 89 kg of methanesulfonic acid (instead of triflic acid), and 7590 kg of water in the procedure of Example 2B.

Part B

About 41.1 grams (0.1 mole) of the N-MeFBSEA, about 5.6 grams (0.017 mole) of octadecyl methacrylate (ODMA, obtained from Sigma-Aldrich, St Louis, MO), 4.2 grams (0.017 mole) of methylacryloxypropyltrimethoxysilane (obtained from Sigma-Aldrich), about 3.3 grams (0.017 mole) of (3-mercaptopropyl)trimethoxysilane (obtained from

Sigma-Aldrich), about 0.1 gram of azo(bis)isobutyronitrile (AIBN), and about 46 grams of ethyl acetate were added to a 250 mL flask equipped with an overhead stirrer, a thermocouple, and a reflux condenser. The mixture was degassed three times using aspirator vacuum and nitrogen pressure. The reaction mixture was heated to about 75 °C under nitrogen for eight hours. Additional AIBN (0.05 gram) was added and heating was continued for another three hours at 75 °C; additional AIBN (0.05 gram) was added and heating was continued at 82 °C for two hours. A clear solution of Copolymer 1 was obtained. The percent solid of the copolymer was about 50% by weight.

Examples 1 and 2

Treatment Composition Preparation:

For Examples 1 and 2, each of $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ and Copolymer 1, respectively, was diluted with a mixture of 70% by weight 2-butoxyethanol and 30% by weight ethanol to make about 200 grams of a 1% by weight treatment solution (Treatment Composition 1 and Treatment Composition 2, respectively). The components were mixed together using a magnetic stirrer and a magnetic stir bar.

Flow Setup and Procedure:

A schematic diagram of a flow apparatus 300 used to determine relative permeability of sea sand or particulate calcium carbonate is shown in Fig. 7. Flow apparatus 300 included positive displacement pump 302 (Model Gamma/4-W 2001 PP, obtained from Protingent AG, Regensburg, Germany) to inject n-heptane at constant rate. Nitrogen gas was injected at constant rate through a gas flow controller 320 (Model DK37/MSE, Krohne, Duisburg, Germany). Pressure indicators 313, obtained from Siemens under the trade designation "SITRANS P" 0-16 bar, were used to measure the pressure drop across a sea sand pack in vertical core holder 309 (20 cm by 12.5 cm²) (obtained from 3M Company, Antwerp, Belgium). A back-pressure regulator (Model No. BS(H)2; obtained from RHPS, The Netherlands) 304 was used to control the flowing pressure upstream and downstream of core holder 309. Core holder 309 was heated by circulating silicone oil, heated by a heating bath obtained from Lauda, Switzerland, Model R22.

The core holder was filled with sea sand (obtained from Aldrich, Bornem, Belgium, grade 60-70 mesh) and then heated to 75 °C. The temperature of 75 °C was maintained for each of the flows described below. A pressure of about 5 bar (5×10^5 Pa) was applied, and the back pressure was regulated in such a way that the flow of nitrogen gas through the sea sand was about 500 to 1000 mL/minute. The initial gas permeability was calculated using Darcy's law.

Synthetic brine according to the natural composition of North Sea brine, was prepared by mixing 5.9% sodium chloride, 1.6% calcium chloride, 0.23% magnesium chloride, and 0.05% potassium chloride and distilled water up to 100% by weight. The brine was then introduced into the core holder at about 1 mL/minute using displacement pump 302.

Heptane was then introduced into the core holder at about 0.5 mL/minute using displacement pump 302. Nitrogen and n-heptane were co-injected into the core holder until steady state was reached.

The treatment composition was then injected into the core holder at a flow rate of 1 mL/minute for about one pore volume. The gas permeability after treatment was calculated from the steady state pressure drop, and improvement factor was calculated as the permeability after treatment/permeability before treatment.

Heptane was then injected for about four to six pore volumes. The gas permeability and improvement factor were again calculated.

For Examples 1 to 2, the liquid used for each injection, the initial pressure (bar), the pressure change (ΔP), the flow rate for each injection, the amount of liquid used for each injection, the flow rate of gas through the core (Q), the gas permeability (K), and the improvement factor (PI) are shown in Table 1, below. The improvement factor is the ratio of the gas permeability after treatment to the gas permeability before treatment.

Table 1

Example	Liquid	Pressure (initial)	ΔP	Flow (mL/min)	Amount Liquid (g)	Q (mL/sec)	K (Darcy)	PI
Ex. 1	none	5.1	0.01	820	none	13.7	37.2	
	brine	5.2	0.08	750	55	12.9	4.5	
	heptane	5.8	0.075	800	50	13.7	4.9	
	Treatment Comp. 1	5.8	0.035	750	100	12.7	10.2	2.1
	heptane	6.0	0.03	800	160	13.6	11.9	2.4
Ex. 2	none	5.2	0.01	580	none	9.7	26.3	
	brine	5.3	0.07	500	50	8.6	3.4	
	heptane	5.3	0.065	500	55	8.5	3.55	
	Treatment Comp. 2	5.7	0.03	520	105	8.8	7.5	2.1
	heptane	5.8	0.03	540	150	9.2	7.6	2.1
Ex. 3	none	5.2	0.01	950	none	16	34.5	
	brine	5.3	0.11	1000	100	16.8	4.1	
	Treatment Comp. 1	5.4	0.06	1200	100	20.4	9.9	2.4
	brine	5.5	0.03	800	400	13.4	12.2	3.0
Ex. 4	none	6.0	0.01	800	none	13.3	36.1	
	brine	6.1	0.065	650	60	10.9	4.5	
	Treatment Comp. 1	6.3	0.02	650	100	14.3	12.9	2.9
	brine	6.6	0.03	850	500	14.3	12.9	2.9
Ex. 5	none	5.9	0.01	820	none	13.6	37.1	
	brine	6.7	0.065	730	200	12.4	5.2	
	Treatment Comp. 2	7.0	0.02	710	170	12.0	15.5	3.0
	brine	6.65	0.03	800	200	13.6	11.6	2.2

Ex. 6	none	4.0	0.01	970	none	16.6	44.0	
	brine	4.1	0.085	470	62	8.2	2.6	
	heptane	4.1	0.08	450	74	7.8	2.5	
	Treatment Comp. 3	4.1	0.04	460	85	7.8	5.7	2.3
	heptane	4.1	0.04	460	238	7.8	4.95	2.0
Ex. 7	none	4.0	0.01	960	none	16.0	43.5	
	brine	4.1	0.08	760	76	13.1	4.7	
	heptane	4.1	0.09	560	70	9.75	3.0	
	Treatment Comp. 4	4.1	0.035	560	91	9.5	7.4	2.5
	heptane	4.1	0.04	570	226	9.7	6.1	2.0
Ex. 8	none	4.0	0.01	930	none	15.5	42.1	
	brine	4.2	0.08	395	208	6.8	2.4	
	Treatment Comp. 3	4.2	0.04	440	160	7.5	5.1	2.1
	brine	4.2	0.05	420	450	7.2	4.0	1.65
Ex. 9	none	3.9	0.01	860	none	14.3	39.0	
	brine	4.0	0.09	770	280	13.4	4.05	
	Treatment Comp. 4	4.0	0.04	770	176	13.1	8.7	2.1
	brine	4.1	0.05	785	580	13.4	7.6	1.9

Examples 3 and 4

Examples 3 and 4 were carried out according to the method of Example 1, with a 1% by weight solution of $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OCH_3)_3$, except that no heptane flows were used.

The liquid used for each injection, the initial pressure (bar), the pressure change (ΔP), the flow rate for each injection, the amount of liquid used for each injection, the flow rate of gas through the core (Q), the gas permeability (K), and the improvement factor (PI) are shown in Table 1, above.

Example 5

Example 5 was carried out according to the method of Example 2, with a 1% by weight solution of Copolymer 1, except that no heptane flows were used.

The liquid used for each injection, the initial pressure (bar), the pressure change (ΔP), the flow rate for each injection, the amount of liquid used for each injection, the flow rate of gas through the core (Q), the gas permeability (K), and the improvement factor (PI) are shown in Table 1, above.

Example 6 and 7

Examples 6 and 7 were carried out according to the method of Examples 1 and 2, with the following modifications. A 2% by weight solution of $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OCH_3)_3$ in 70/30 2-butoxyethanol/ethanol was prepared to make Treatment Composition 3 for Example 6, and a 2% by weight solution of Copolymer 1 in 70/30 2-butoxyethanol/ethanol was prepared to make Treatment Composition 4 for Example 7. Particulate calcium carbonate (obtained from Merck, Darmstadt, Germany as granular marble, particle size in a range from 0.5 mm to 2 mm) was used instead of sea sand.

The liquid used for each injection, the initial pressure (bar), the pressure change (ΔP), the flow rate for each injection, the amount of liquid used for each injection, the flow rate of gas through the core (Q), the gas permeability (K), and the improvement factor (PI) are shown in Table 1, above.

Example 8 and 9

Examples 8 and 9 were carried out according to the method of Examples 1 and 2, except using Treatment Composition 3 and Treatment Composition 4, respectively, described in Examples 6 and 7. Particulate calcium carbonate (obtained from Merck, Darmstadt, Germany as granular marble, particle size in a range from 0.5 mm to 2 mm) was used instead of sea sand, and no heptane flows were used.

The liquid used for each injection, the initial pressure (bar), the pressure change (ΔP), the flow rate for each injection, the amount of liquid used for each injection, the

flow rate of gas through the core (Q), the gas permeability (K), and the improvement factor (PI) are shown in Table 1, above.

Example 10

A sandstone core cut from a sandstone obtained from Cleveland Quarries, Vermillion, OH, under the trade designation "BEREA SANDSTONE" was treated with a solution of 12% by weight $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 3% by weight acetic acid, 10% by weight water, and 75% by weight ethanol using the following method. Referring now to flow apparatus 400 shown in Fig. 8, the core 408 was placed in a hydrostatic core holder 409 with an overburden pressure of 1000 psi (6.9×10^6 Pa). The core holder was enclosed in an oven 410. The temperature was raised gradually to 140 °C, and then 5 pore volumes of the treatment solution through an inlet of the core holder at a rate of 1.5 mL/minute through regulator 403 using liquid metering pump 402 while maintaining an outlet pressure of 200 psi (1.4×10^6 Pa) using back pressure regulator 404. The treatment solution was maintained in the core for 15 hours at 140 °C and 200 psi (1.4×10^6 Pa). The core was then washed with brine (1% by weight aqueous sodium chloride) for 20 pore volumes and flushed with nitrogen from gas regulator 420 connected to nitrogen tank 422. An adsorption of 7.35 milligrams/gram (mg/g) was calculated by measuring the weight of the core before and after treatment. The adsorption is the weight increase of the core after treatment over the weight of the treated core. A contact angle versus n-decane of 60° was measured on the surface of the core.

The treated core was tested for spontaneous oil imbibition by hanging the nitrogen-flushed core under an electronic balance and submerging in n-decane 24 °C. The weight of the core was recorded regularly over the course of 300 minutes. The imbibition is reported as a percentage of n-decane saturation of the core and was found to be about 10% after 10 minutes and 40% after 300 minutes. For comparison an untreated sandstone core was tested for spontaneous oil imbibition using the same procedure. The n-decane saturation was found to be about 60% after 10 minutes. The results are shown in Fig. 1.

Example 11

Example 11 was carried out using the method of Example 10 except a treatment solution of 4% by weight $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 3% by weight acetic acid,

10% by weight water, and 83% by weight ethanol was used. An adsorption of 0.6 mg/g was calculated. A contact angle versus n-decane of 60° was measured on the surface of the core. The treated core was tested for spontaneous oil imbibition, and the n-decane saturation was found to be about 40% after 10 minutes and about 55% after 300 minutes. The results are shown in Fig. 1.

Comparative Example A

Comparative Example A was carried out using the method of Example 10 except a treatment solution described in Example 1 of U. S. Pat. Pub. No. 2008/0113882 (Arco et al.) was used. The treated core was tested for spontaneous oil imbibition, and the n-decane saturation was found to be about 50% after 10 minutes and about 65% after 100 minutes. The results are shown in Fig. 1.

Example 12

Example 12 was carried out using the method of Example 10, except crude oil was injected into the core for two pore volumes at 140 °C and 200 psi (1.4×10^6 Pa) before the treatment solution was injected. A contact angle versus n-decane of 60° was measured on the surface of the core.

Example 13

Example 13 was carried out using the method of Example 10 except a treatment solution of 6% by weight $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 1% by weight acetic acid, and 93% by weight of a hydrocarbon solvent obtained from BJ Services Company, Houston, TX, under the trade designation "PARAVAN" was used. Also, water was injected into the core for two pore volumes at 140 °C and 200 psi (1.4×10^6 Pa), and then nitrogen was injected for 10 pore volumes before the treatment solution was injected. An adsorption of 25.1 mg/g was calculated. A contact angle versus n-decane of 60° was measured on the surface of the core. The treated core was tested for spontaneous oil imbibition, and the n-decane saturation was found to be about 10% after 10 minutes and about 20% after 300 minutes. The results for oil imbibition for Example 13, Example 10, and an untreated core are shown in Fig. 2.

Example 14

Example 14 was carried out using the method of Example 10 except a treatment solution of 6% by weight $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 1% by weight acetic acid, and 93% by weight of a hydrocarbon solvent obtained from BJ Services Company under the trade designation "PARAVAN" was used. Also, water was injected into the core for two pore volumes at 140 °C and 200 psi (1.4×10^6 Pa), and then nitrogen was injected for 10 pore volumes before the treatment solution was injected. An adsorption of 12.4 mg/g was calculated.

Instead of the spontaneous oil imbibition, a single phase oil injection was carried out on the treated core and an untreated core. Referring again to Fig. 8, the nitrogen flushed core 408 was placed in the core holder 409 in an oven 410 at 140 °C with an overburden pressure of 1000 psi (6.9×10^6 Pa). n-Decane was injected at 2 mL/minute using liquid metering pump 402, and the initial pressure and pressure drop across the core were measured with pressure transducers 413. The pressure drop was recorded over a number of pore volumes. The results are shown in Fig. 3.

Example 15

Example 15 was carried out using the method of Example 10 except a treatment solution of 6% by weight $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 1% by weight acetic acid, and 93% by weight diesel was used. Also, water was injected into the core for two pore volumes at 140 °C and 200 psi (1.4×10^6 Pa), and then nitrogen was injected for 10 pore volumes before the treatment solution was injected. An adsorption of 6.5 mg/g was calculated.

Instead of the spontaneous oil imbibition, a single phase oil injection was carried out on the treated core and an untreated core using the method described in Example 14. The results are shown in Fig. 4.

Example 16

Example 16 was carried out using the method of Example 10 except a treatment solution of 6% by weight $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 1% by weight acetic acid, and 93% by weight diesel was used. Also, water was injected into the core for two pore volumes at 140 °C and 200 psi (1.4×10^6 Pa), and then nitrogen was injected for 10 pore

volumes before the treatment solution was injected. A reservoir core obtained from Petroleum Development Oman having an initial permeability of about 0.1 mD was used instead of a sandstone obtained under the trade designation "BEREA SANDSTONE". An adsorption of 3.1 mg/g was calculated, and the absolute permeability was measured and determined to decrease by 11%.

Instead of the spontaneous oil imbibition, a single phase oil injection was carried out on the treated core and an untreated core using the method described in Example 14 except n-decane was injected at 0.5 mL/minute. The results are shown in Fig. 5.

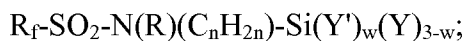
Various modifications and alterations of this disclosure may be made by those skilled the art without departing from the scope and spirit of the disclosure, and it should be understood that this disclosure is not to be unduly limited to the illustrative embodiments set forth herein.

What is Claimed is:

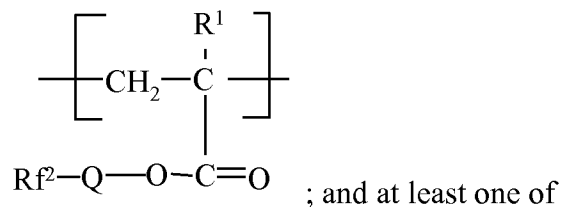
1. A method of treating a hydrocarbon-bearing formation, the method comprising:

contacting the hydrocarbon-bearing formation with a treatment composition, the treatment composition comprising solvent and a fluorinated silane, wherein the fluorinated silane is selected from the group consisting of:

(a) a fluorinated silane represented by formula



(b) a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by



(i) a second divalent unit comprising a pendent $-Si(Y')_w(Y)_{3-w}$ group;

or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-Si(Y')_w(Y)_{3-w}$ group; and

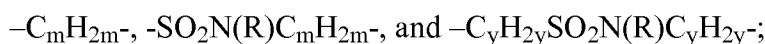
(c) combinations thereof;

wherein

R_f is fluoroalkyl having up to 6 carbon atoms;

each R_f^2 is independently fluoroalkyl having up to 6 carbon atoms;

each Q is independently selected from the group consisting of



m and n are each independently in a range from 1 to 11;

each y is independently in a range from 1 to 6;

R is selected from the group consisting of hydrogen, alkyl having one to eight carbon atoms, and aryl;

each R^1 is independently hydrogen or methyl;

each Y is independently a hydrolyzable group;

each Y' is independently a non-hydrolyzable group; and

each w is independently 0, 1, or 2;

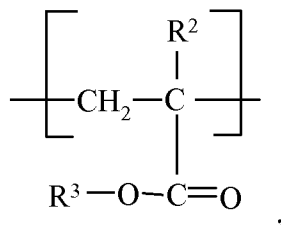
wherein the method does not include intentionally fracturing the hydrocarbon-bearing formation.

2. The method of claim 1, wherein R_f is perfluorobutyl, R is alkyl having one to four carbon atoms, and n is an integer from 2 to 6.

3. The method of claim 2, wherein the fluorinated silane is $C_4F_9SO_2N(CH_3)(CH_2)_3Si(OR')_3$, wherein each R' is independently selected from the group consisting of methyl and ethyl.

4. The method of claim 1, wherein R_f^2 is perfluorobutyl, Q is $-SO_2-N(R)-C_mH_{2m}-$, wherein R is alkyl having one to four carbon atoms, and m is an integer from 2 to 6.

5. The method of claim 4, wherein the nonionic compound further comprises at least one third divalent unit represented by formula:



wherein

each R^2 is independently selected from the group consisting of hydrogen and methyl; and

each R^3 is independently alkyl having from 1 to 30 carbon atoms.

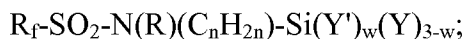
6. The method of any preceding claim, wherein the solvent comprises at least one of water, an alcohol, ketone, glycol, glycol ether, hydrofluoroether, or hydrocarbon.

7. The method of claim 6, wherein the solvent comprises at least one of methanol, ethanol, propanol, butanol, 2-butoxyethanol, or propylene glycol.

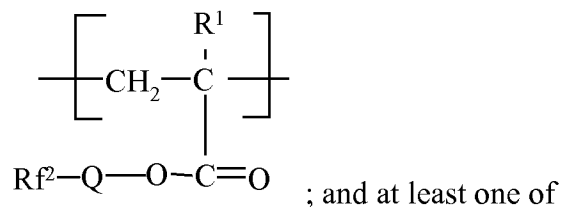
8. The method of claim 6, wherein the solvent comprises at least one of kerosene, diesel, gasoline, pentane, hexane, heptane, mineral oil, or a naphthene.
9. The method of claim 6, wherein the solvent comprises a ketone having from 4 to 10 carbon atoms or a hydrofluoroether.
10. The method of any one of claims 1 to 5, further comprising:
 - receiving data comprising a temperature and a brine composition of the hydrocarbon-bearing formation; and
 - selecting a treatment composition for the hydrocarbon-bearing formation comprising the fluorinated silane and the solvent, wherein, at the temperature, a mixture of the brine composition and the treatment composition separates into at least two separate transparent liquid layers, and wherein the mixture is free of precipitated solid.
11. The method of any preceding claim, wherein the treatment composition further comprises an acidic compound selected from the group consisting of acetic acid, citric acid, formic acid, trifluoromethanesulfonic acid, perfluorobutyric acid, hydroboric acid, sulfuric acid, phosphoric acid, hydrochloric acid, and combinations thereof, or wherein the treatment composition further comprises an alkaline compound selected from the group consisting of an amine, an alkali metal hydroxide, an alkaline earth metal hydroxide, and combinations thereof.
12. The method of any preceding claim, wherein the hydrocarbon-bearing formation is an oil-bearing formation.
13. The method of any preceding claim, further comprising contacting the hydrocarbon-bearing formation with a fluid before contacting the hydrocarbon-bearing formation with the composition, wherein the fluid at least one of at least partially solubilizes or partially displaces at least one of brine or liquid hydrocarbons in the hydrocarbon-bearing formation.

14. A composition comprising a hydrocarbon-bearing formation and a fluorinated compound bonded to the hydrocarbon-bearing formation, wherein the fluorinated compound is selected from the group consisting of:

(a) a fluorinated silane represented by formula



(b) a nonionic compound free of alkyleneoxy groups and comprising at least one first divalent unit represented by



(i) a second divalent unit comprising a pendent $-Si(Y')_w(Y)_{3-w}$ group;

or (ii) a monovalent unit comprising a thioether linkage and at least one terminal $-Si(Y')_w(Y)_{3-w}$ group;

(c) combinations thereof; and

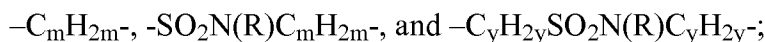
(d) condensation products thereof;

wherein

R_f is fluoroalkyl having up to 6 carbon atoms;

each Rf^2 is independently fluoroalkyl having up to 6 carbon atoms;

each Q is independently selected from the group consisting of



m and n are each independently in a range from 1 to 11;

each y is independently in a range from 1 to 6;

R is selected from the group consisting of hydrogen, alkyl having one to eight carbon atoms, and aryl;

each R^1 is independently hydrogen or methyl;

each Y is independently a hydrolyzable group;

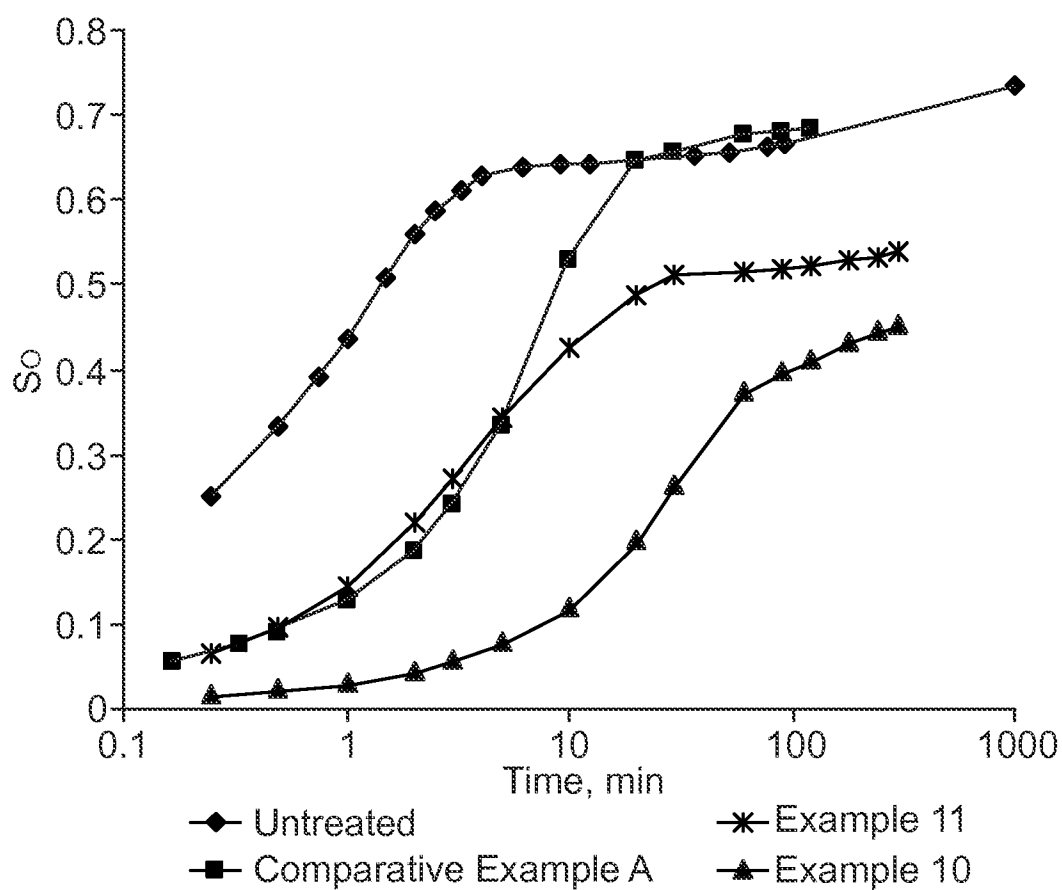
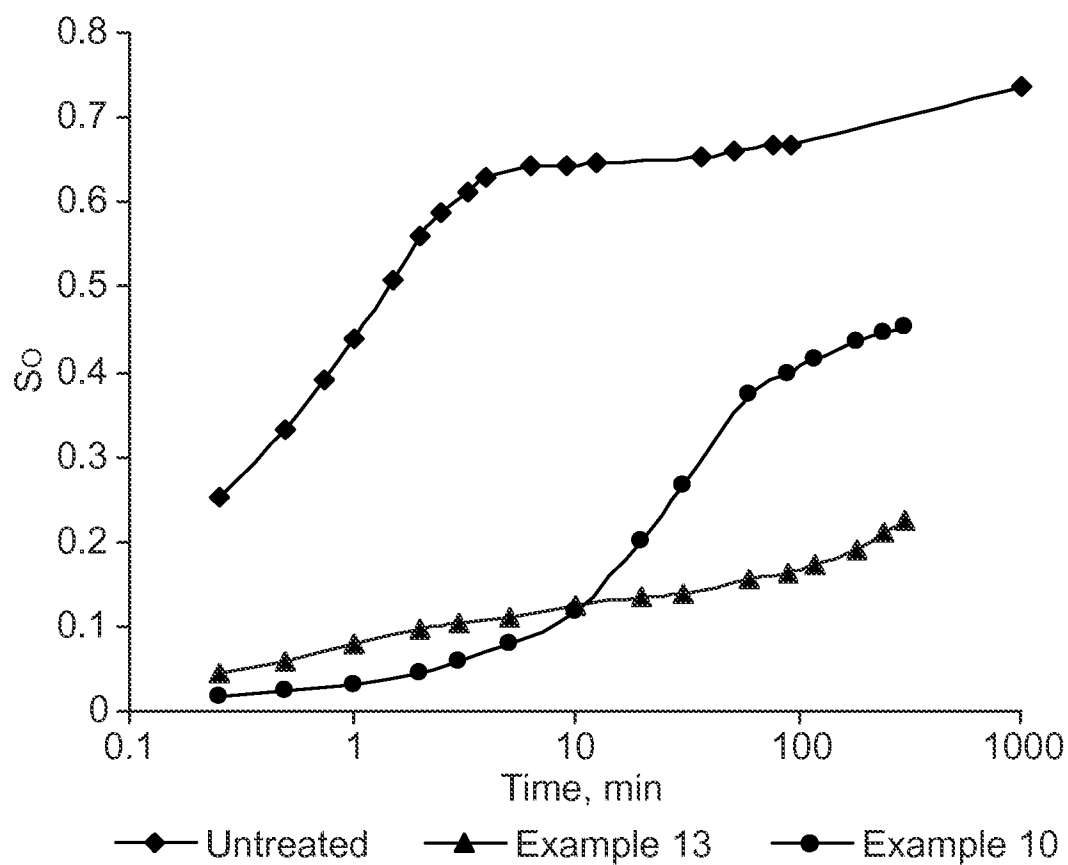
each Y' is independently a non-hydrolyzable group; and

each w is independently 0, 1, or 2;

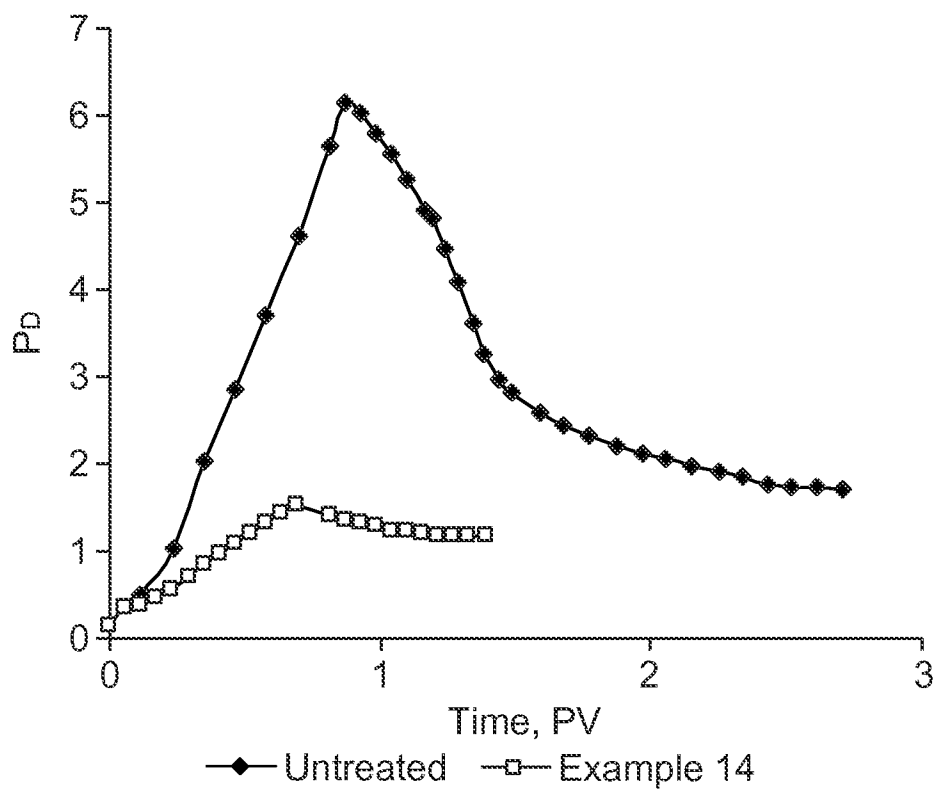
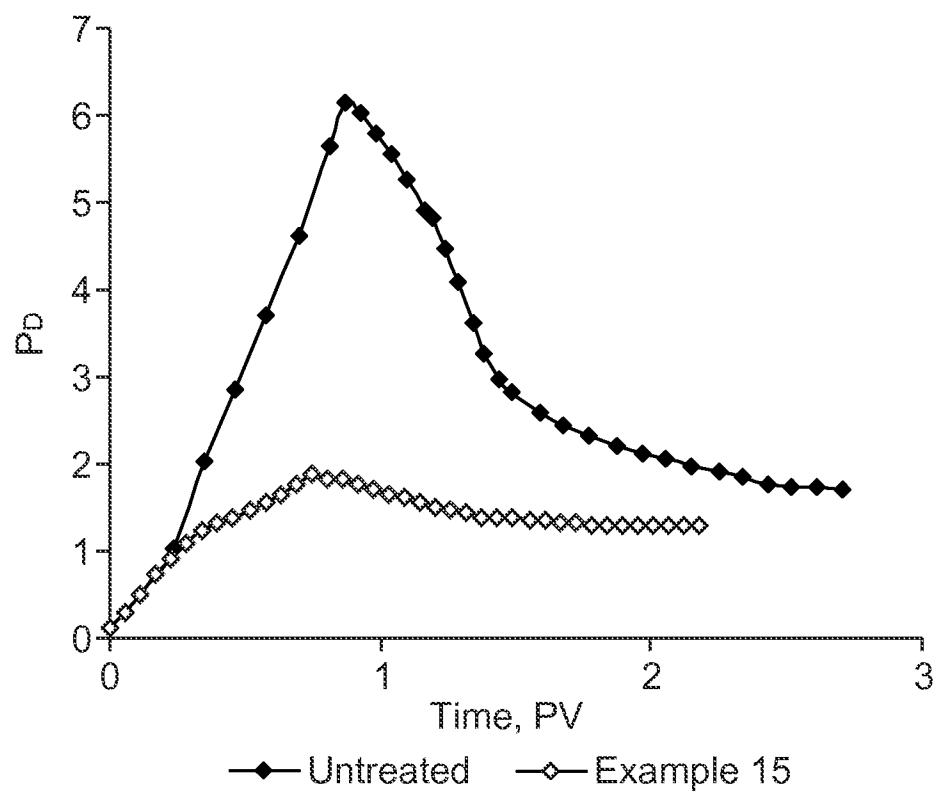
wherein the hydrocarbon-bearing formation is free of manmade fractures.

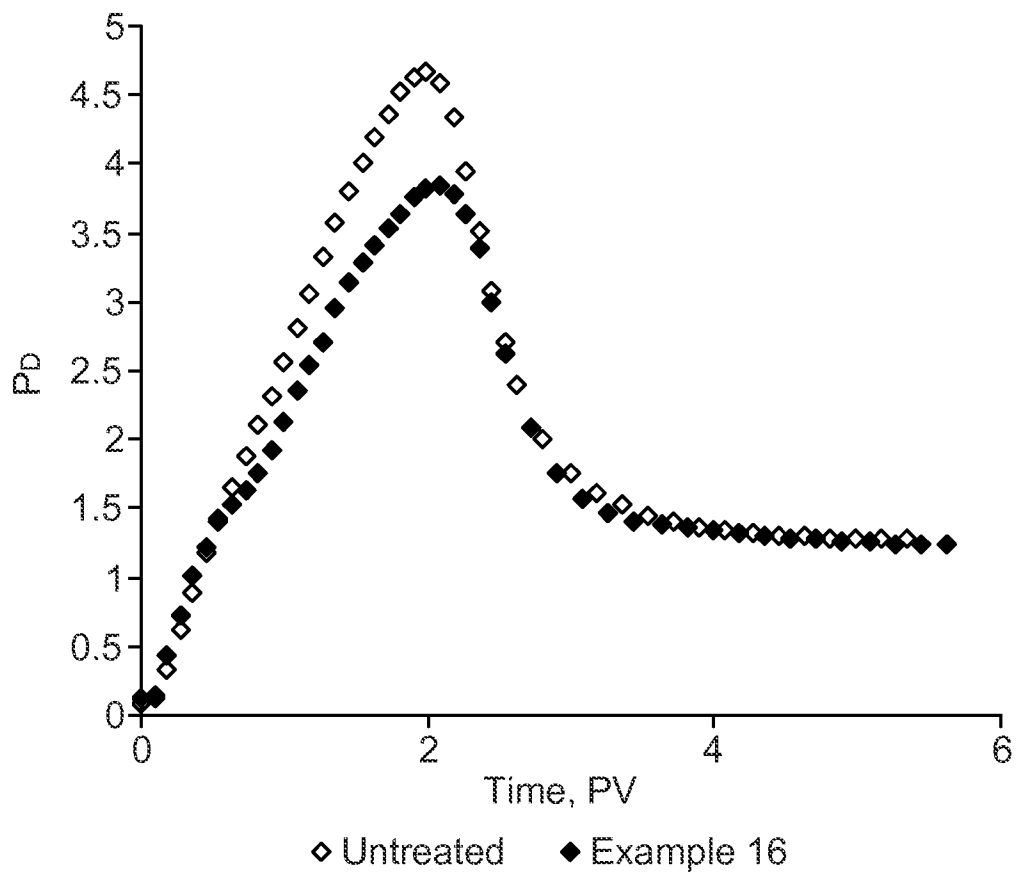
15. The composition of claim 14, wherein the fluorinated compound shares at least one siloxane bond with the hydrocarbon-bearing formation.

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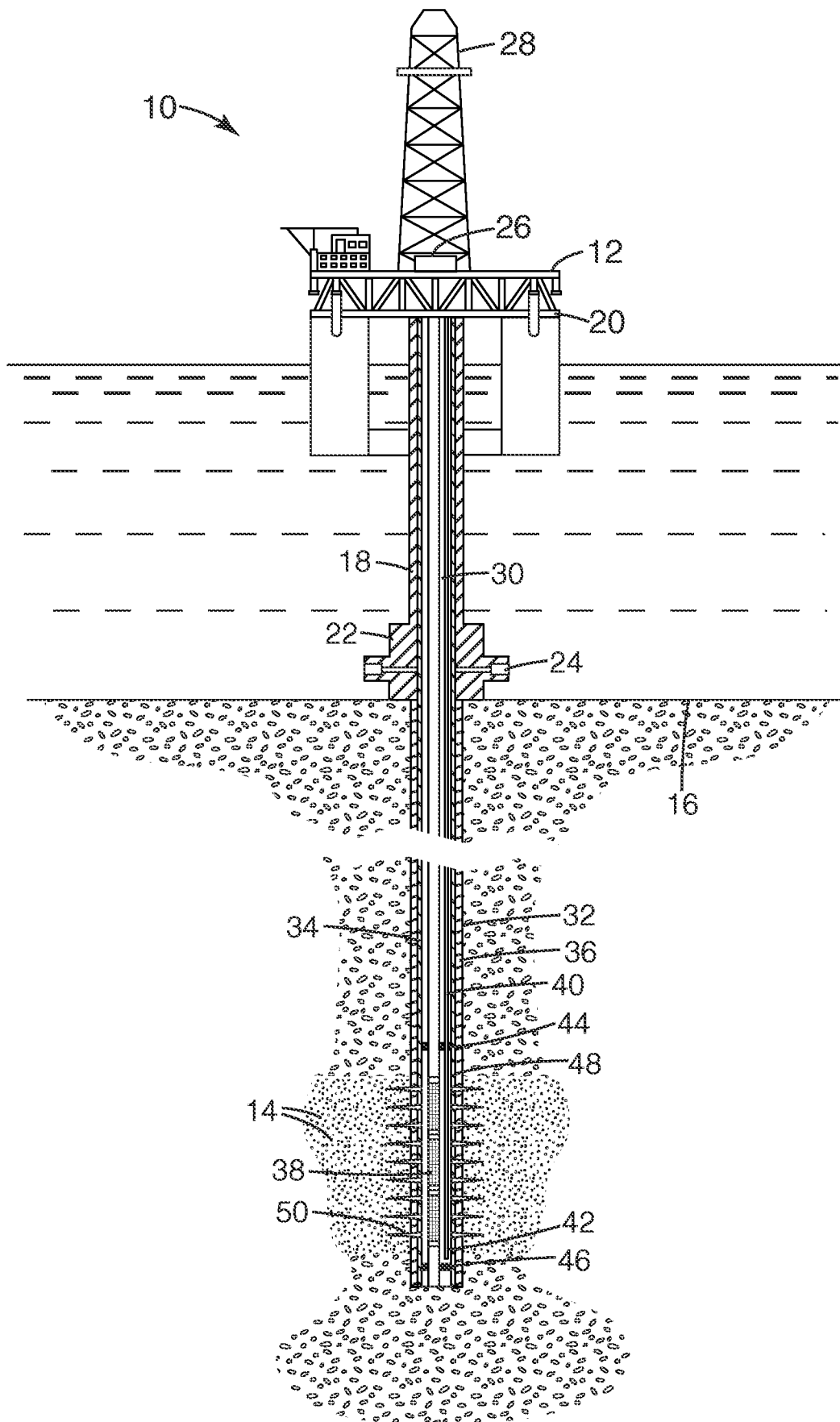
*Fig. 1**Fig. 2*

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*Fig. 3**Fig. 4*

*Fig. 5*

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*Fig. 6*

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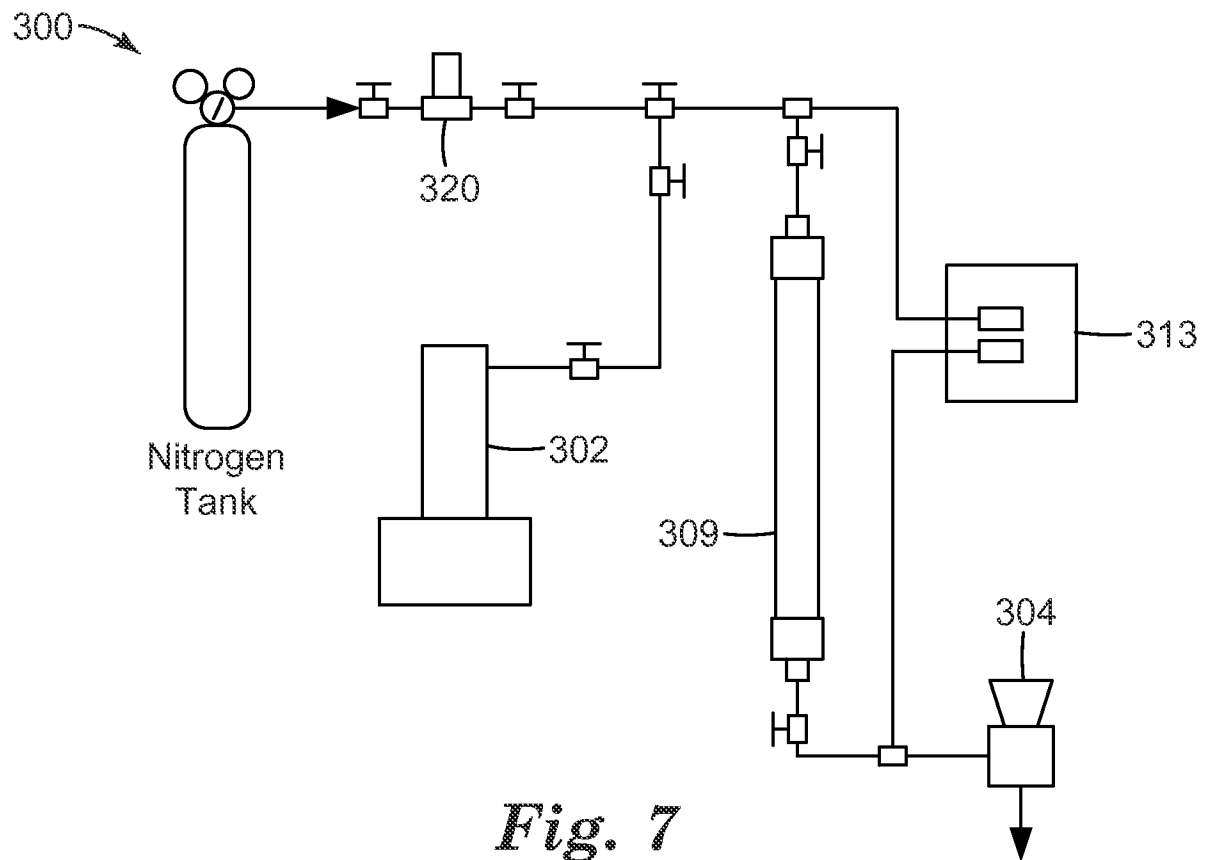


Fig. 7

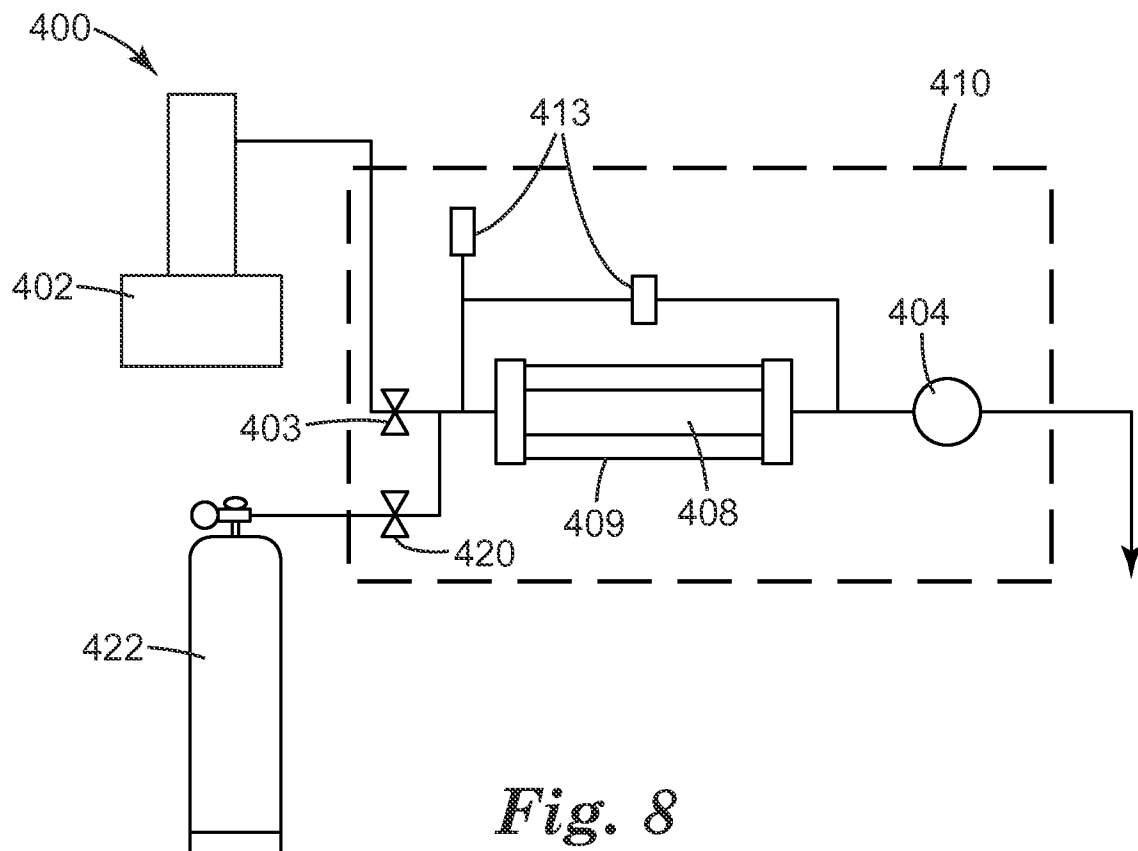


Fig. 8