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(54) Title: VISCOELASTIC-SURFACTANT FRACTURING FLUIDS HAVING OXIDIZER

(57) Abstract: A method and hydraulic fracturing fluid that is a viscoelastic surfactant (VES) fracturing fluid having a surfactant and an inorganic oxidizer salt for hydraulic fracturing of a geological formation. The VES fracturing fluid is provided through a wellbore into the geological formation to hydraulically fracture the geological formation to form hydraulic fractures in the geological formation. The method includes oxidizing organic material in the hydraulic fractures with the VES fracturing fluid.

VISCOELASTIC-SURFACTANT FRACTURING FLUIDS HAVING OXIDIZER

CLAIM OF PRIORITY

[0001] This application claims priority to U.S. Provisional Application No.
5 62/955,717, filed December 31, 2019, the entire contents of which are
incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This disclosure relates to hydraulic fracturing.

BACKGROUND

10 **[0003]** Hydraulic fracturing employs fluid and material to generate fractures
in a geological formation to stimulate production from oil and gas wells.
Hydraulic fracturing is a well-stimulation technique in which rock is fractured by
a pressurized fluid that may be a fracturing fluid. The process can involve the
pressure injection of fracturing fluid into a wellbore to generate cracks in the
15 deep-rock formations through which natural gas, petroleum, and brine will flow
more freely. The fracturing typically generates paths that increase the rate at
which production fluids, such as crude oil or natural gas, can be produced from
the reservoir formations. The amount of increased production may be related
to the amount of fracturing. Proppant may be employed to maintain the
20 fractures as pressure depletes in the well during hydrocarbon production. The
proppant may resist formation closure stresses to keep fractures open.

[0004] Hydraulic fracturing may allow for the recovery of crude oil and
natural gas from unconventional formations that geologists once believed were
impossible to produce. Unconventional source rocks may be organic-rich
25 sedimentary deposits, such as shales and mud rocks. The organic
components of the source shale may include hydrocarbon-source material
kerogen and its produced components bitumen and pyrobitumen.

SUMMARY

[0005] An aspect relates to a method of hydraulic fracturing. The method includes providing a viscoelastic surfactant (VES) fracturing fluid having a surfactant and an inorganic oxidizer salt through a wellbore into a geological formation to hydraulically fracture the geological formation to form hydraulic fractures in the geological formation. The method includes oxidizing organic material in the hydraulic fractures with the VES fracturing fluid.

[0006] Another aspect relates to a method including pumping a reactive VES fracturing fluid having a surfactant and an inorganic oxidizer salt through a wellbore into a geological formation for hydraulic fracturing of the geological formation. The method includes forming hydraulic fractures in the geological formation with the reactive VES fracturing fluid. Further, the method includes oxidizing organic material in the hydraulic fractures with the reactive VES fracturing fluid. The method includes generating a permeable channel through organic material at a fracture face of a hydraulic fracture between the geological formation and the hydraulic fracture via oxidizing of the organic material at the fracture face with the reactive VES fracturing fluid.

[0007] Yet another aspect relates a reactive VES fracturing fluid for hydraulic fracturing of a geological formation. The reactive VES fracturing fluid includes a surfactant at a concentration in the reactive VES fracturing fluid in a range of 0.1 weight percent (wt%) to 10 wt%. The reactive VES fracturing fluid includes an inorganic oxidizer salt for the reactive VES fracturing fluid to degrade kerogen in the geological formation.

[0008] Yet another aspect relates to a reactive VES fracturing fluid for hydraulic fracturing of a subterranean formation. The reactive VES fracturing fluid includes water and a surfactant at a concentration in the reactive VES fracturing fluid in a range of 0.5 wt% to 7 wt%. The reactive VES fracturing fluid includes an inorganic oxidizer salt for the reactive VES fracturing fluid to oxidize kerogen in the subterranean formation to fragment the kerogen.

[0009] Yet another aspect relates to a method of applying a reactive VES-based fluid. The method includes providing the reactive VES-based fluid

having a surfactant and an inorganic oxidizer salt through a wellbore into a subterranean formation. The concentration of the inorganic oxidizer salt in the reactive VES-based fluid is in a range of 1 wt% to 20 wt%. The method includes oxidizing organic material in the subterranean formation with the reactive VES-based fluid.

[0010] The details of one or more implementations are set forth in description and in the accompanying drawings. Other features and advantages will be apparent from the description, drawings, and the claims.

BRIEF DESCRIPTION OF DRAWINGS

[0011] FIG. 1 is a diagram of a well including a wellbore formed in a geological formation having organic matter, such as kerogen.

[0012] FIG. 2 a diagram of the well of FIG. 1 after a hydraulic fracture is formed and with the well in production.

[0013] FIG. 3 is a diagram of micellization in which surfactant molecules in aqueous solution form into a colloidal structure that is a surfactant micelle.

[0014] FIG. 4 is a diagram of micelle shapes (types).

[0015] FIG. 5 is a diagram of exemplary chemical structures of zwitterionic surfactants that may be a surfactant in the reactive viscoelastic surfactant (VES)-based fluid.

[0016] FIG. 6 is a diagram of exemplary chemical structures of cationic surfactants that may be a surfactant in the reactive VES-based fluid.

[0017] FIG. 7 is a diagram of exemplary chemical structures of anionic surfactants that may be a surfactant in the reactive VES-based fluid.

[0018] FIG. 8 is a diagram of exemplary chemical structures of nonionic surfactants that may be a surfactant in the reactive VES-based fluid.

[0019] FIG. 9 is a diagram of a well system having a wellbore formed through the Earth surface into a geological formation in the Earth crust.

[0020] FIG. 10 is a method of hydraulic fracturing a geological formation having organic material.

[0021] FIG. 11 is Table 1 giving solution parameters for the three VES fluid samples prepared for viscosity measurement in Example 1.

[0022] FIG. 12 is a plot of viscosity and temperature over time for the three VES fluid samples in Example 1.

[0023] FIG. 13 is Table 2 giving solution parameters for the three VES fluids prepared with the polymer additive FP9515SH for viscosity measurement in Example 2.

[0024] FIG. 14 is a plot of viscosity and temperature over time for the three VES fluid samples in Example 2.

DETAILED DESCRIPTION

[0025] Some aspects of the present disclosure are directed to hydraulic fracturing fluids that are viscoelastic surfactant-based and bear an oxidizing component(s) (oxidizer). The hydraulic fracturing fluid includes a viscoelastic surfactant (VES) that forms micelles to increase viscosity of the hydraulic fracturing fluid as a VES-based fluid. The increase in viscosity may be beneficial for conveying of proppant by the VES-based hydraulic fracturing fluid.

[0026] A first salt may be added to the VES-based hydraulic fracturing fluid to drive formation of the micelles. The first salt may be, for example, a monovalent or divalent salt. A second salt (for example, an inorganic oxidizer salt) may be added as an oxidizing component of the VES-based hydraulic fracturing fluid to give a reactive VES-based hydraulic fracturing fluid. This second salt as an oxidizer may provide for attack of organic material (for example, kerogen) in the geological formation treated by the reactive VES-based hydraulic fracturing fluid. The second salt may also further promote formation of micelles in the VES-based hydraulic-fracturing fluid. Both the first salt (monovalent or divalent) and the second salt (oxidizer) are inert to oxidation.

[0027] In certain embodiments, the first salt (monovalent or divalent salt) is not added to the reactive VES-based hydraulic-fracturing fluid. Instead, the second salt (oxidizer) provides for the formation of the micelles. In some embodiments, a polymer may be optionally added to reactive VES-based hydraulic-fracturing fluid to enhance the increase in viscosity. In

implementations, the second salt (and first salt if included) may act as a breaker of the viscosity of the reactive VES-based hydraulic-fracturing fluid with or without a polymer loading.

[0028] In some applications, the VES-based fluid containing oxidative materials (for example, oxidizer salt) may be pumped as a stand-alone hydraulic fracturing treatment to fracture the geological formation and transport proppant. The VES-based fluid containing oxidative materials and proppant may be pumped alternatively with VES-based fluid containing oxidative materials and no proppant as a hybrid treatment. The VES-based fracturing fluid may be pumped as part of a channel fracturing operation. Channel fracturing may refer to hydraulic fracturing treatment employing intermittent pumping of proppant-laden fluid and proppant-free fluid to generate conductive channels within the formation.

[0029] In other embodiments, the VES-based fluid containing oxidative materials is pumped alternatively with carbon dioxide (CO₂)-based fluids that optionally contain oxidizers for breaking down kerogen. A benefit may be that CO₂ slugs can enhance the delivery of oxidizer to the kerogen and better expel hydrocarbons from the geological formation. If employed, the CO₂-based fluid with oxidizer may contain organic oxidizers, reactive gases, or in-situ forming halogens, or any combinations of these. The CO₂-based fluid with oxidizer may be foamed in some instances.

[0030] The VES-based hydraulic-fracturing fluid may be pre-mixed, for example, in a batch mix vessel and then pumped downhole through a wellbore in a geological formation for the hydraulic fracturing of the geological formation. The amount of components (for example, surfactant or oxidizer salt) added to the mix vessel (for example, a batch mix vessel) may be adjusted in response to the hydraulic-fracturing conditions and the amount of kerogen or other organic matter in the subterranean region of the geological formation being treated. In certain embodiments, at least some of the surfactant or oxidizer salt is added to a conduit on the discharge of the pump conveying the VES-based hydraulic-fracturing fluid. The amount of the

oxidizer salt added to the conduit (or to the mix vessel) may be adjusted (for example, in real time) in response to the hydraulic-fracturing conditions and the amount of kerogen or other organic matter in the fractures of the geological formation.

5 **[0031]** It should be understood that the phrase “VES fluid” as utilized in the present disclosure generally refers to a “VES-based fluid” in that the fluid contains more than a VES. Similarly, the phrase “VES hydraulic fracturing fluid” generally refers to a VES-based hydraulic fracturing fluid” in that the hydraulic fracturing fluid contains more than a VES. Further, a VES-based
10 fluid having the VES may include water as a base fluid.

[0032] While the present discussion may at times focus on the VES-based fluid as a VES-based hydraulic fracturing fluid, the present VES-base fluid may also be a VES-based treatment fluid for treatments other than hydraulic fracturing. The other treatments may be independent (or separate) from
15 hydraulic fracturing or in combination with hydraulic fracturing.

Implementations of treatments with the VES-based treatment fluid include: (1) degradation of filter cake during open hole drilling or during hydraulic fracturing; (2) upgrading oil in the subterranean formation (geological formation) by reducing the viscosity and boiling point of the oil; (3) breaking
20 organic matter (for example, paraffin, bitumen, or oil) in the subterranean formation by reducing the viscosity of the organic matter; and (4) oxidizing organic scale (buildup) in a subterranean formation to remove (clean-up) the organic scale to promote subsequent fluid injection into the subterranean formation for the wellbore employed in an injection well.

25 **[0033]** Production from unconventional source-rock formations has become economically viable. The technology for accessing these reservoirs continues to advance as the industry improves drilling, completion, and stimulation techniques. Unconventional source-rock reservoirs differ from conventional reservoirs at least due to the presence of the hydrocarbon source material,
30 such as kerogen and kerogen-produced components, in unconventional source-rock reservoirs. This hydrocarbon source material as irregular organic

matter can represent 5-10 weight percent (wt%) [or 10-20 volume percent (vol%)] of the sedimentary source-rock formation. An assortment of minerals are woven and compacted together with the organic matter (for example, kerogen) resulting in a complex hierarchical structure with toughness and strength characteristics similar to other natural materials. The tensile characteristics of the organic matter have been demonstrated by nanoindentation of organic-rich shale micro/nano-cantilever source-shale beams tested under a scanning electron microscope (SEM). The chemomechanical characteristics of the organic matter implicate a problematic role of the organic matter in the tensile stresses in hydraulic fracturing and in overall mechanical and chemical operational success of the fracturing. The interwoven organic matter that the fracturing fluid encounters as the fracture extends into the source rock formation is further discussed with respect to FIG. 1.

[0034] FIG. 1 is well 100 having a wellbore 102 formed in a geological formation 104 having organic matter 106 (organic material), such as kerogen. The wellbore 102 is depicted as a circular cross section. The geological formation 104 is a subterranean formation in the Earth's crust and may be an unconventional source-rock formation having hydrocarbon. The geological formation 104 may be an organic-rich shale zone. The spider-web symbol represents the presence of the organic matter 106.

[0035] In FIG. 1, a fracture 108 is being formed via injection of a fracturing fluid 110 (stimulation fluid) from the Earth's surface through the wellbore 102 into the geological formation 104. The fracturing fluid 110 may be injected at a specified flow rate (q_0). The flow rate (q_0) may be specified as a volumetric flow rate or mass flow rate. The fracturing fluid 110 may include proppant 112, such as sand or ceramic proppant. The fracture 108 may propagate perpendicular to a minimum principal stress 114 of the formation 104 and in a direction against a maximum principal stress 116 of the formation.

[0036] The schematic in FIG. 1 depicts the hydraulic fracture 108 extending from the wellbore 102. The fracturing fluid 110 system encounters the ductile

organic matter 106 illustrated as spider webs. The presence of the organic matter 106 at the fracture face 118 may restrict the generation of permeable channels from the geological formation 104 into the fracture 108. Thus, the organic matter 106 may inhibit the subsequent production of hydrocarbon from the formation 104 into and through the fracture 108 to the wellbore 102 and Earth surface. The fracture face 118 may be an interface of the forming fracture 108 with the geological formation 104. Conventional hydraulic-fracturing stimulation fluids typically do not address challenges of fracturing organic-rich shale zones. The polymer-like organic material 106 may be intertwined within the organic material and with the rock. The organic material 106 affects fracturing (fracture) behavior and reduces resulting hydraulic conductivity.

[0037] Hydraulic fracturing fluids may include polymers or crosslinkers for viscosifying the fracturing fluids as proppant-carrying fluids. Developments in fracturing fluids (or stimulation fluid chemicals) have also included additives, such as polymer breakers, biocides, clay swelling inhibitors, and scale inhibitors. VES-based hydraulic fracturing fluids may be a cleaner alternative to polymer-based systems.

[0038] Among the most commonly-used fracturing fluids for unconventional formations are slickwater systems incorporating friction-reducing synthetic polymer that facilitates the pumping of stimulation fluids at large rates (for example, at least 100 barrels per minute). Moreover, the incorporation of gas into fracturing fluids may reduce water as a component of the fracturing fluid.

[0039] To address the challenge of improving hydraulic fracturing in unconventional source-rock reservoirs, embodiments of the present techniques include reactive fluids that can break down the polymer nature of the organic matter 106 on the hydraulic fracture faces 118. At the fracture face 118, organic matter 106 (for example, kerogen) is beneficially cracked open due to exposure to oxidizing conditions (for example, aqueous oxidizing conditions). Techniques to implement the oxidizing conditions via a fracturing fluid 110 include, for example: (1) inorganic oxidizers in aqueous fluids, (2)

inorganic and organic oxidizers in carbon dioxide (CO₂), (3) inorganic or organic oxidizers in foamed mixtures of water and CO₂, and (4) reactive gases in CO₂.

[0040] FIG. 2 is a well 200 that is the well 100 of FIG. 1 after the hydraulic fracture 108 is formed and with the well 200 in production. FIG. 2 depicts the hydraulic fracture 108 extending from the wellbore 102. The fracture 108 has a length 202 and width 204. The fracturing fluid 110 (FIG. 1) that formed the fracture 108 was a VES fracturing fluid having an oxidizer that attacked the organic matter 106. Thus, the fracturing fluid 110 system caused organic matter 106 to crack open to generate permeable channels from the formation 104 into the fracture 108 and therefore provide for conductivity from the formation 104 through the fracture 108 to the wellbore 102. The well 200 as depicted is in production phase with produced hydrocarbon 206 flow from the geological formation 104 through the fracture 108 and wellbore 102 to the Earth surface. The flow rate of the produced hydrocarbon 206 may be labeled as Q_0 and may be characterized as a volumetric flow rate or mass flow rate.

[0041] As discussed, VES-based systems may be combined with reactive fluid components for breaking down organic matter 106, such as kerogen, in the geological formation 104. This fracturing-fluid system may also be utilized to upgrade heavy oil or clean-up organic residues.

[0042] VES-based fluids generally differ from conventional polymer-based fracturing fluid systems. Polymer-based fracturing fluids typically incorporate a water-soluble polymer, crosslinker, and breaker. A viscous polymer-based fluid (for example, a gel at greater than 10 centipoise [cP]) is pumped into a geological formation and with the fluid gel transporting proppant into a fracture network. Then, the gel is broken by enzyme or oxidizer and the fluid flowed back from the formation to the surface. This process may be operationally complex in relying on polymer hydration and a variety of additives, such as biocides, crosslinkers, and breakers. By contrast, viscoelastic surfactants may be simpler to utilize in the field because typically there is no hydration step and because fewer additives may be included. For example, in the case of

breakers, VES-based fluids can break in the formation by changes in brine concentration due to contact with produced fluids or alternatively by contact with hydrocarbons which disrupt the surfactant micelles of the VES-based fluid.

5 **[0043]** An advantage of VES- based fluids over polymer-based systems can be that VES- based fluids may typically be solids-free (except for any proppant). Therefore, in implementations, the VES- based fluids generally do not deposit residue in the geological formation or on the proppant pack. Thus, VES-based fluids may be more efficient than polymer-based systems in
10 hydraulic-fracture reservoir stimulation because the conductivity of the in-place proppant pack affects well productivity.

[0044] In addition, VES-based fluids may heal after exposure to shear. Additives may further improve the shear re-healing time of the VES-based fluid gel. A benefit of healing may be that viscosity is maintained for conveying
15 proppant. The self-healing may restore the micelles and hence the viscosity. The VES fluid experiences shear forces during pumping at the wellhead. The viscosity may be restored as the VES fluid goes into the wellbore and formation and thus perform hydraulic fracturing and convey proppant. Crosslinked polymer fluids, by contrast, can be irreversibly damaged during
20 pumping because the shear forces cause some of the covalent bonds to break. The micelles of the VES fluid are not covalently held together and their formation is reversible. This may be an advantage of VES over crosslinked polymer for hydraulic fracturing.

[0045] Embodiments employ VES gels to hydraulically fracture
25 unconventional source-rock formations. These gels may contain a specified amount of oxidizer that can break down organic material (for example, kerogen) in the subterranean formation. Thus, embodiments may combine the benefits of viscoelastic surfactants as fracturing fluids with the reactive capabilities of an oxidizer component to break down kerogen on the surface of
30 the fractures. The reactive VES fluid may also be utilized to upgrade heavy oil (for example, bitumen or including bitumen) by breaking down the heavy oil

and reducing viscosity of the heavy oil. Heavy oil may be crude oil having an American Petroleum Institute (API) gravity less than 20°. The reactive VES fluid may also be utilized to clean downhole by removing organic residues from the surface of the rock formation deposited as a result of drilling, completion, and fracturing. The reactive VES fluid may dissolve filter cake in open-hole completions (both water injectors and hydrocarbon producers).

[0046] A purpose of the viscoelastic surfactant (for example, cationic, anionic, nonionic, zwitterionic or amphoteric, or a combination of cationic and anionic surfactants) is to form micelles to increase viscosity of the fluid to give the VES-based fluid. Cylindrical (truncated) or wormlike micelles give greater fluid viscosity than spherical micelles. Spherical micelles generally do not produce viscosity. Truncated cylindrical micelles may make worm-like or rod-like micelles that entangle to give viscosity. VES-based systems may include a surfactant capable of forming a wormlike micelle that can entangle and thus impart viscosity to the fluid. The fluid system typically includes salt to drive formation of the micelles, such as worm-like micelles that entangle. VES-based fluids may also contain a breaker to disrupt the micelles and reduce the viscosity while in the formation to enhance flowback.

[0047] Surfactant selection may be an aspect of formulating a VES-based fracturing fluid. Under certain conditions, surfactant molecules arrange into colloidal structures called micelles as indicated earlier. With these structures, the hydrocarbon tails of the surfactants orient toward each other while the polar head groups form an interface with the surrounding aqueous media.

[0048] FIG. 3 depicts micellization 300 in which surfactant molecules 302 in aqueous solution form into a colloidal structure that is a surfactant micelle 306. The surfactant molecules 302 are a hydrocarbon chain having a polar head group 308 and a hydrocarbon tail 310. Surfactant micelles 306 form 304 spontaneously in aqueous solution when the surfactant concentration, c , exceeds the threshold referred to as the critical micelle concentration (cmc). The size and structure of the micelles 306 may be controlled by the selected charge and geometry of the surfactant molecules 302. The size and structure

of the micelles 306 may be controlled by solution conditions, such as concentration of the surfactant molecules, type and concentration of salt, temperature, ionic strength, and shear rate.

[0049] FIG. 4 gives examples 400 of micelle shapes (types). Depicted are
 5 a spherical micelle 402, a cylindrical (worm-like) micelle 404, a vesicles (bilayer) micelle 406, and a lamellar micelle 408. For each micelle type, the respective qualitative prediction of shape may be based on the packing parameter.

[0050] The molecular packing parameter may provide for insight into the
 10 self-assembly phenomenon of the surfactant micelle as an aggregate. The molecular packing parameter is defined as $v_0/a l_0$, where v_0 and l_0 are the volume and the length of the surfactant tail and a is the surface area of the hydrophobic core of the aggregate expressed per molecule in the aggregate (here referred to as the area per molecule). For instance, for a spherical
 15 micelle with a core radius R , made up of g molecules, the volume of the core $V = g v_0 = 4\pi R^3/3$ and the surface area of the core $A = g a = 4\pi R^2$. Hence, $R = 3v_0/a$ from simple geometrical relations. If the micelle core is packed with surfactant tails without empty space, then the radius R cannot exceed the extended length l_0 of the tail. Introducing this constraint in the expression for R
 20 gives $0 \leq v_0/a l_0 \leq 1/3$, for spherical micelles.

[0051] For spherical, cylindrical, or bilayer aggregates made up of g surfactant molecules, the geometrical relations for the volume V and the surface area A are given in Table 1. The variables V , A , and g in the table refer to the entire spherical aggregate, unit length of a cylindrical aggregate, or unit
 25 area of a bilayer aggregate, respectively, for the three shapes. These geometrical relations together with the constraint that at least one dimension of the aggregate (the radius of the sphere or the cylinder, or the half-bilayer thickness, all denoted by R) cannot exceed l_0 lead to the following connection between the molecular packing parameter and the aggregate shape: $0 \leq v_0/a l_0 \leq 1/3$ for sphere, $1/3 \leq v_0/a l_0 \leq 1/2$ for cylinder, and $1/2 \leq v_0/a l_0 \leq 1$ for bilayer.
 30 Therefore, if the molecular packing parameter is known, the shape and size of

the equilibrium aggregate can be readily identified. This is the predictive sense of the molecular packing parameter.

Table 1. Geometrical Relations for Spherical, Cylindrical, and Bilayer

5 Aggregates

Variable	Sphere	Cylinder	Bilayer
volume of core $V = gv_0$	$4\pi R^3/3$	πR^2	$2R$
surface area of core $A = ga$	$4\pi R^2$	$2\pi R$	2
area per molecule a	$3v_0/R$	$2v_0/R$	v_0/R
packing parameter v_0/al_0	$v_0/al_0 \leq 1/3$	$v_0/al_0 \leq 1/2$	$v_0/al_0 \leq 1$
largest aggregation number $g_{\max}$	$4\pi l_0^3/3v_0$	$\pi l_0^2/v_0$	$2l_0/v_0$
aggregation number g	$g_{\max}(3v_0/al_0)^3$	$g_{\max}(2v_0/al_0)^2$	$g_{\max}(v_0/al_0)$

[0052] Variables V , A , g , and $g_{\max}$ refer to the entire spherical aggregate, unit length of a cylinder or unit area of a bilayer. R is the radius of spherical or cylindrical micelle or the half-bilayer thickness of the spherical vesicle. v_0 and l_0 are the volume and extended length of the surfactant tail. The variable $g_{\max}$ is the largest aggregation number possible for the given geometry based on the constraint that the aggregate core is filled and the tail cannot stretch beyond its extended length.

[0053] Changes to the surfactant molecule or solution conditions influence the micelle structure. Surfactant molecules with polar head groups that are large (for example, greater than 8 carbons) may promote the formation of spherical micelles. Surfactant molecules with polar head groups that are small (for example, less than 8 carbons) should encourage lamellae formation. For instance, nonionic surfactants with small ethylene-oxide head groups (small number of carbons, $m < 8$) should favor bilayer and lamellae structures. However, nonionic surfactants with larger head groups (for example, $m=10$, 12, 14, or 16) may yield cylindrical or wormlike micelles. Further, salt addition to ionic surfactant solutions generally causes a transition from spherical to

cylindrical micelles. For example, the cationic surfactant hexadecyltrimethylammonium bromide (also referred to as cetyltrimethylammonium bromide or CTAB) forms spherical micelles in aqueous solution. Upon addition of sodium nitrate (NaNO_3) to the surfactant solution, the spherical micelles transform into wormlike micelles.

[0054] In addition to surfactant selection, formulation of the present VES-based fracturing fluid may further include salt selection, oxidizer selection, and selection of any polymer loading. The salts utilized may interact electrostatically with the polar head groups and thereby reduce head group repulsion. This may cause a structural change to the micelle to ideally form wormlike micelles that can entangle with one another and cause the viscosity of the VES-based fracturing fluid to increase. A wide range of salts are capable of interacting in this manner. These salts can include monovalent or divalent salts. Salts that are inert to oxidation may be desired.

[0055] As for oxidizer selection, the oxidizers employed in this application should demonstrate reactivity toward kerogen. To this end, salts of chlorate and bromate are examples. Both are reactive toward kerogen. Further, both alkali and alkaline earth metal salts are suitable. The oxidizers employed should be nonreactive towards the surfactant molecules in the fracturing fluid at ambient and reservoir temperatures for the time period of pumping so that the fluid can maintain viscosity throughout the pumping time. Alternatively, oxidizers may be selected that are instead (or also) reactive towards heavy oil or organic residues in the formation so that this reactive VES fluid could be utilized for upgrading oil or well cleanup.

[0056] With respect to polymer loading, polymers are commonly used in hydraulic fracturing fluids to create viscosity. However, such polymers are known to damage the formation. A traditional VES fluid is advantageous in its lack of polymer additives. This makes VES fluids less damaging to the formation. However, in present embodiments, the oxidizing salt in the reactive VES fluid gives the fluid the capacity to “break” including to break polymers in the VES fluid. Thus, in certain implementations, polymer can be added to the

reactive VES fluid to boost viscosity of the VES fluid and increase efficacy of the fracturing operation without inflicting damage to the formation. The polymer added may include, for example, acrylamide acrylic acidic copolymer, polyvinyl pyrrolidone, polyethylene oxides, and natural polymers. The
5 acrylamide acrylic acidic copolymer may be 2-acrylamido-2-methylpropane sulfonic acid (AMPS). Natural polymers added may include guar, xanthan gum, and cellulose.

[0057] Embodiments of the reactive VES-based fluid for hydraulic fracturing include water and surfactant to form the VES-based fluid. The majority (>90
10 volume %) of the fluid is water. The amount of VES used for the fluid can range 4-8 volume % depending on the temperature and viscosity requirement. The hydraulic fracturing fluid as a reactive VES-based fluid includes an inorganic oxidizer salt. The inorganic oxidizer salt is included as an oxidizer or reactive component for the reactive VES-based fluid to attack organic matter in
15 the subterranean formation. The inorganic oxidizer salt may also promote micelle formation for increased viscosity of the reactive VES fluid. The VES-based fluid may additionally include a monovalent or divalent salt that promotes micelle formation and is generally not an oxidizer. The reactive VES-based fluid may include organic compounds, such as phthalic acid,
20 salicylic acid, or their salts. Other fluid additives in the reactive VES-based fluid may include a breaker, corrosion inhibitor, scale inhibitor, biocide, or pH buffer, or any combinations of these. The reactive VES-based fluid may include inorganic oxidizer salt as the sole salt to promote micelle formation and not include the monovalent salt or divalent salt.

[0058] The reactive VES-based fluid (hydraulic fracturing fluid) may have a concentration of the surfactant, for example, in a range of 0.1 weight percent (wt%) to 10 wt% or in a range of 0.5 wt% to 7 wt%, or at least 1 wt%. The surfactant may be, for example, a zwitterionic or amphoteric surfactant, a cationic surfactant, an anionic surfactant, a nonionic surfactant, or a
30 combination of cationic and anionic surfactants.

[0059] The zwitterionic surfactant may be a betaine, phosphobetaine, or sultaines. The zwitterionic surfactant may include dihydroxyl alkyl glycinate, alkyl ampho acetate or propionate, alkyl amidoamine oxide, gemini VES, alkyl betaine, alkyl amidopropyl betaine, and alkylimino mono- or di-propionates
5 derived from waxes, fats, or oils.

[0060] FIG. 5 depicts exemplary structures 500 of a zwitterionic surfactant that may be the surfactant in the reactive VES-based fluid. These structures 500 include disodium tallowiminodipropionate 502, disodium oleamidopropyl betaine 504, and erucylamidopropyl betaine 506. For the
10 tallowiminodipropionate 502, R = tallow.

[0061] FIG. 6 depicts specific structures 600 of a cationic surfactant that may be the surfactant in the reactive VES-based fluid. These exemplary structures 600 for the cationic surfactant are alkylammonium salts and include oleyl methyl bis(2-hydroxyethyl)ammonium chloride 602, erucyl bis(2-
15 hydroxyethyl)methylammonium chloride 604, and N,N,N, trimethyl-1-octadecammonium chloride 604. Other alkylammonium salts as the cationic surfactant may include, for example, cetyltrimethylammonium bromide (CTAB) or dimethylene-1,2-bis(dodecyldimethylammonium bromide). The cationic surfactant can be associated with inorganic anions, such as sulfate, nitrate,
20 and halide. The cationic surfactant can be associated with organic anions, such as salicylate, functionalized sulfonates, chlorobenzoates, phenates, picolates, and acetates. The cationic surfactant can alternatively be associated with an oxidizing anion, such as chlorate, bromate, perchlorate, chlorite, hypochlorite, persulfate, iodate, bromite, perborate, dichromate,
25 permanganate, ferrate, percarbonate, nitrite, and nitrate.

[0062] Anionic surfactants for the reactive VES-based hydraulic fracturing fluid may include alkyl sarcosinates or sulfonates. FIG. 7 gives exemplary structures 700 of anionic surfactants that may be the surfactant in the VES hydraulic fracturing fluid. Oleoyl sarcosine 702 is an example of an alkyl
30 sarcosinate. In implementations, the oleoyl sarcosine 702 may constitute about 94% of the sarcosinate product that is the surfactant. Methyl ester

sulfonate 704 and sodium xylene sulfonate 704 are examples of sulfonates. For the methyl ester sulfonate 704 structure, R is an alkyl chain with 10-30 carbon atoms,

[0063] Nonionic surfactants for the reactive VES-based hydraulic fracturing fluid may include amine oxides. Referring to FIG. 8, the amine oxide gelling agents have the structure 800 where R is an alkyl or alkylamido group averaging from about 8 to 27 carbon atoms and each R' is independently H, or an alkyl group averaging from about 1 to 6 carbon atoms. In implementations, R is an alkyl or alkylamido group averaging from about 8 to 16 carbon atoms and R' are independently alkyl groups averaging from about 2 to 3 carbon atoms. In a particular implementation, the amino oxide gelling agent is tallow amido propylamine oxide (TAPAO). Major components of the tallow amido substituent are palmitic acid 802, stearic acid 804, and oleic acid 806.

[0064] The reactive VES hydraulic fracturing fluid may include monovalent or divalent salts at a concentration in a range of 0 wt% to 50 wt%, in a range of 1 wt% to 50 wt%, in a range of 0 wt% to 15 wt%, in a range of 1 wt% to 15 wt%, or less than 15 wt%. These salts may promote micelle formation, such as wormlike or cylindrical micelles, to increase viscosity of the fracturing fluid. These monovalent or divalent salts may include lithium fluoride (LiF), sodium fluoride (NaF), potassium fluoride (KF), magnesium fluoride (MgF₂), calcium fluoride (CaF₂), strontium fluoride (SrF₂), barium fluoride (BaF₂), lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), strontium chloride (SrCl₂), barium chloride (BaCl₂), lithium bromide (LiBr), sodium bromide (NaBr), potassium bromide (KBr), magnesium bromide (MgBr₂), calcium bromide (CaBr₂), strontium bromide (SrBr₂), and barium bromide (BaBr₂).

[0065] The reactive VES hydraulic fracturing fluid includes inorganic oxidizer salts in concentrations in a range of 1 wt% to 20 wt% or in a range of 1 wt% to 10 wt%. The concentration may generally be more including at the greater end of these ranges or greater (for example, 3 wt% to 20 wt% or 5 wt% to 25 wt%) for implementations where other salt (for example, a monovalent or

divalent salt) is not included in the formulation for micelle formation. These inorganic oxidizer salts are an oxidizer or reactive component for the VES hydraulic fracturing fluid to attack and degrade organic material in the geological formation. The inorganic oxidizer salts are typically generally inert to oxidation. The oxidizer salts may include lithium chlorate (LiClO_3), sodium chlorate (NaClO_3), potassium chlorate (KClO_3), magnesium chlorate [$\text{Mg}(\text{ClO}_3)_2$], calcium chlorate [$\text{Ca}(\text{ClO}_3)_2$], strontium chlorate [$\text{Sr}(\text{ClO}_3)_2$], barium chlorate [$\text{Ba}(\text{ClO}_3)_2$], lithium bromate (LiBrO_3), sodium bromate (NaBrO_3), potassium bromate (KBrO_3), magnesium bromate [$\text{Mg}(\text{BrO}_3)_2$], calcium bromate [$\text{Ca}(\text{BrO}_3)_2$], strontium bromate [$\text{Sr}(\text{BrO}_3)_2$], and barium bromate [$\text{Ba}(\text{BrO}_3)_2$]. Other oxidizers may include magnesium peroxide, calcium peroxide, sodium nitrate, sodium nitrite, sodium persulfate, potassium persulfate, sodium tetraborate, sodium percarbonate, sodium hypochlorite, an iodate salt, a periodate salt, a dichromate salt, and a permanganate salt. The iodate salt may be a salt of IO_3^- with lithium, sodium, potassium, magnesium, etc. Hydrogen peroxide as an oxidizer may also be used.

[0066] The inorganic oxidizer salts may promote formation of micelles, such as cylindrical or worm-like micelles, to increase viscosity of the fracturing fluid. Thus, both the inorganic oxidizer salt and the aforementioned monovalent or divalent salt may promote micelle formation. The combined concentration of the inorganic oxidizer salt and the monovalent or divalent salt in the VES hydraulic fracturing fluid may be at least 1 wt%, at least 3 wt%, at least 5 wt%, at least 7 wt%, at least 10 wt%, or at least 12 wt%, or at least 15 wt%. For implementations where a monovalent or divalent salt is not included in the formulation, the concentration of the inorganic oxidizer salt in the reactive VES hydraulic fracturing fluid may be at least 3 wt%, at least 5 wt%, at least 7 wt%, or at least 10 wt%. These concentrations of the inorganic oxidizer may also be employed with the presence of a monovalent or divalent salt.

[0067] As mentioned, the reactive VES-based fluid may include organic compounds, such as phthalic acid, salicylic acid, or their salts. The salicylate or other ion in the presence of the surfactant may cause the viscoelastic gel to

form. The acid (nonionic) form of these compounds causes the viscoelasticity development to be delayed until the pH is altered (raised) and the anion is released. For example, the pH may be raised by adding urea that is hydrolyzed as the solution starts to heat after pumping into the wellbore and formation. This is a way of imparting some control over when the viscoelasticity develops. In some cases, carboxylic acid and the -OH group in salicylic acid interacts with the quaternary ammonium group of VES and acts as a crosslinker to link and make the micelles more robust. This aids formation of stable micelles and thus stable viscosity at formation temperatures. As also mentioned, other fluid additives in the reactive VES-based fluid may include a breaker, corrosion inhibitor, scale inhibitor, biocide, or pH buffer, or any combinations of these.

[0068] FIG. 9 is a well site 900 having a wellbore 902 formed through the Earth's surface 904 into a geological formation 906 in the Earth's crust. The geological formation 906 may be labeled as a subterranean formation, a rock formation, or a hydrocarbon formation. The geological formation 906 may be an unconventional formation to be subjected to hydraulic fracturing.

[0069] The wellbore 902 can be vertical, horizontal, or deviated. The wellbore 902 can be openhole but is generally a cased wellbore. The annulus between the casing and the formation 906 may be cemented. Perforations may be formed through the casing and cement into the formation 906. The perforations may allow both for flow of fracturing fluid into the geological formation 906 and for flow of produced hydrocarbon from the geological formation 906 into the wellbore 902.

[0070] The well site 900 may have a hydraulic fracturing system including a source 908 of fracturing fluid 910 at the Earth surface 904 near or adjacent the wellbore 902. The source 108 may include one or more vessels holding the fracturing fluid 910. The fracturing fluid 110 may be stored in vessels or containers on ground, on a vehicle (for example, truck or trailer), or skid-mounted. The fracturing fluid 910 may be a water-based fracturing fluid. In some implementations, the fracturing fluid 910 is slickwater that may be

primarily water (for example, at least 98.5% water by volume). The fracturing fluid 910 can be prepared from seawater. The fracturing fluid 910 can also be gel-based fluids. The fracturing fluid 910 can include polymers and surfactants. Other additives to the fracturing fluid 910 may include

5 hydrochloric acid, friction reducer, emulsion breaker, emulsifier, temperature stabilizer, and crosslinker. Fracturing fluids 910 of differing viscosity may be employed in the hydraulic fracturing. The fracturing fluid 910 may include proppant. In the illustrated embodiment, the fracturing fluid 910 is a reactive VES-based fracturing fluid for at least a portion of the hydraulic fracturing

10 operation.

[0071] The hydraulic fracturing system at the well site 900 may include motive devices such as one or more pumps 912 to pump (inject) the fracturing fluid 910 through the wellbore 902 into the geological formation 906. The pumps 912 may be, for example, positive displacement pumps and arranged

15 in series or parallel. Again, the wellbore 902 may be a cemented cased wellbore and have perforations for the fracturing fluid 910 to flow (injected) into the formation 906. In some implementations, the speed of the pumps 910 may be controlled to give desired flow rate of the fracturing fluid 910. The system may include a control component to modulate or maintain the flow of fracturing

20 fluid 910 into the wellbore 902 for the hydraulic fracturing. The control component may be, for example, a control valve(s). In some implementations, as indicated, the control component may be the pump(s) 912 as a metering pump in which speed of the pump 912 is controlled to give the desired or specified flow rate of the fracturing fluid 910. The set point of the control

25 component may be manually set or driven by a control system, such as the control system 914.

[0072] The fracturing fluid 910 may be prepared (formulated and mixed) offsite prior to disposition of the fracturing fluid 910 into the source 908 vessel at the well site 900. Alternatively, a portion (some components) of the

30 fracturing fluid 910 may be mixed offsite and disposed into the source 908 vessel and the remaining portion (remaining components) of the fracturing fluid

910 added to the source 908 vessel or to a conduit conveying the fracturing fluid 910. In other implementations, the fracturing fluid 908 may be prepared onsite with components added to (and batch mixed in) the source 908 vessel.

[0073] For embodiments of the fracturing fluid 910 as a reactive VES-based fracturing fluid, the fracturing fluid 910 in the source 908 vessel may have all components of the fracturing fluid 910. In certain embodiments, some components of the fracturing fluid 910 may be added to the source 908 vessel near or at the time (or during) the pumping of the fracturing fluid 910 into the wellbore 902 for the hydraulic fracturing. However, in other embodiments, not all components of the fracturing fluid 910 are include in the source 908 vessel. Instead, at least one component of the fracturing fluid 910 is be added to the conduit conveying the fracturing fluid 910 either on the suction of the pump 912 or discharge of the pump 912, or both, as the fracturing fluid 910 is being pumped into the wellbore 902.

[0074] An additive or component 916 may be added to the fracturing fluid 908. For the reactive VES-based fracturing fluid, the component 916 may be, for example, surfactant or the inorganic oxidizer salt. The concentration of the component 916 (for example, inorganic oxidizer salt) in the fracturing fluid 910 may be maintained or adjusted by modulating a flow rate (mass or volume) of addition of the component 916 via a control device 918. The set point of the control device 918 may be manually set or specified (directed) by the control system 914. The control device 918 may be a control valve on the conduit conveying component 916 to the source 908 (for example, vessel) of the fracturing fluid 910. For the component 916 as the inorganic oxidizer salt, the inorganic oxidizer salt may be added as a solid (powder), for example, via the control device 918 as a rotary feeder valve. Alternatively, the inorganic oxidizer salt may in added in an aqueous dispersion to the fracturing fluid 910 in the source 908 vessel. Moreover, instead of adding the component 916 to the source 108 vessel, the component 916 may be added to the discharge conduit of the pump 912 as the pump 912 is providing the fracturing fluid 910 into the wellbore 902.

[0075] The hydraulic fracturing system at the well site 900 may have a source of proppant, which can include railcars, hoppers, containers, or bins having the proppant. Proppant may be segregated by type or mesh size (particle size). The proppant can be, for example, sand or ceramic proppants.

5 The source of proppant may be at the Earth surface 904 near or adjacent the wellbore 902. The proppant may be added to the fracturing fluid 910 such that the fracturing fluid 910 includes the proppant. In some implementations, the proppant may be added (for example, via gravity) to a conduit conveying the frac fluid 110, such as at a suction of a fracturing fluid pump 912. A feeder or
10 blender may receive proppant from the proppant source and discharge the proppant into pump 912 suction conduit conveying the fracturing fluid 110.

[0076] The fracturing fluid 910 may be a slurry having the solid proppant. The pump 912 discharge flow rates (frac rates) may include a slurry rate which may be a flow rate of the fracturing fluid 910 as slurry having proppant. The
15 pump 912 discharge flow rates (frac rates) may include a clean rate which is a flow rate of fracturing fluid 910 without proppant. In particular implementations, the fracturing system parameters adjusted may include at least pump(s) 912 rate, proppant concentration in the frac fluid 910, component 916 addition rate, and component 916 concentration in the
20 fracturing fluid 910. Fracturing operations can be manual or guided with controllers.

[0077] The well site 900 may include a control system 914 that supports or is a component of the hydraulic fracturing system. The control system 914 includes a processor 920 and memory 922 storing code 924 (logic,
25 instructions) executed by the processor 920 to perform calculations and direct operations at the well site 900. The processor 920 may be one or more processors and each processor may have one or more cores. The hardware processor(s) 920 may include a microprocessor, a central processing unit (CPU), a graphic processing unit (GPU), a controller card, or other circuitry.
30 The memory may include volatile memory (for example, cache and random access memory (RAM)), nonvolatile memory (for example, hard drive, solid-

state drive, and read-only memory (ROM)), and firmware. The control system 914 may include a desktop computer, laptop computer, computer server, programmable logic controller (PLC), distributed computing system (DSC), controllers, actuators, control cards, an instrument or analyzer, and a user interface. In operation, the control system 914 may facilitate processes at the well site 900 and including to direct operation of aspects of the hydraulic fracturing system.

[0078] The control system 914 may be communicatively coupled to a remote computing system that performs calculations and provides direction.

The control system 914 may receive user input or remote-computer input that specifies the set points of the control device 916 or other control components in the hydraulic fracturing system. The control system 914 may specify the set point of the control device 918 for the component 916 addition. In some implementations, the control system 914 may calculate or otherwise determine the set point of the control device 118. The determination may be based at least in part on the operating conditions of the hydraulic fracturing and on information (or feedback) regarding the amount of kerogen in the region of the geological formation 906 being hydraulically fractured.

[0079] The fracturing fluid as a VES-based fluid containing oxidative materials may be applied (pumped) without other hydraulic fracturing fluids employed in the hydraulic fracturing. In other words, the VES-based fluid containing oxidative materials (for example inorganic oxidizer salt) may be pumped as a stand-alone hydraulic fracturing treatment to fracture the formation and to transport proppant. However, the VES-based fluid may also be applied (pumped) in tandem (in a sequence) with other fluids including other hydraulic fracturing fluids.

[0080] The VES-based fluid containing oxidative materials and proppant may be pumped alternatively with VES-based fluid containing oxidative materials and no proppant as a hybrid treatment. The VES-based fracturing fluid may also be pumped as part of conductivity channel fracturing. In other applications, the VES-based fluid containing oxidative materials may be

pumped as part of a slickwater hydraulic fracturing operation in which the VES fluid is the proppant-laden fluid in the sequence. In certain implementations, the slickwater includes oxidizer for breaking down kerogen. The slickwater may be pumped before and after the VES fluid in the hydraulic fracturing. In certain cases, VES fluid is pumped first followed by slickwater fluid or other viscosified fluid so that when the VES fluid enters microfractures, the VES fluid generally does not damage the formation as slick water polymers can leave residue. The other viscosified fluid may include, for example, a fracturing fluid viscosified via a polymer.

10 **[0081]** The VES-based fluid containing oxidative materials may be pumped alternatively with CO₂-based fluids. A benefit of employing a CO₂-based fracturing fluid in tandem with the reactive VES-based fracturing fluid is that CO₂ slugs can promote expulsion of hydrocarbons from the formation. Further, CO₂-based fracturing fluid may include an oxidizer to break down organic material (kerogen) in the formation. CO₂ slugs may enhance delivery of oxidizer to the kerogen. The oxidizer in the CO₂-based fluid may be an organic oxidizer that is soluble in organic solutions or non-polar media (solvents) because the CO₂-based fracturing fluid may generally be non-polar. These “organic oxidizers” may include an organic cation and an oxidizer inorganic anion. The oxidizer inorganic anion may be, for example, chlorate or bromate. Other oxidizer inorganic anions of the organic oxidizers may include persulfate, perborate, percarbonate, hypochlorite, peroxide, or iodate.

25 **[0082]** Another implementation of a CO₂-based fracturing fluid that may be sequenced with the reactive VES-based fracturing fluid is a foam emulsion (oxidizer foam) including CO₂ (or other inert gas), water, and oxidizer to break down the kerogen in the formation during hydraulic fracturing. A benefit may include reduction of water use. Another benefit may be the effect of the inert gas (CO₂) on hydrocarbon recovery in displacement of hydrocarbons from the kerogen-laden formation. The oxidizer(s) in the foam may be at least one of an inorganic oxidizer and an organic oxidizer, which may reside in different phases of the foam, respectively.

30

[0083] Yet another implementation of a CO₂-based fracturing fluid that may be sequenced with the reactive VES-based fracturing fluid is supercritical CO₂ fracturing fluid. The supercritical CO₂ may have reactive oxidizer gases (for example, bromine, chlorine, chlorine dioxide, or ozone) for the treatment of kerogen-containing rocks to enhance hydraulic fracturing efficiency of unconventional source rock formations. The reactive oxidizer gases may chemically degrade kerogen to enhance rock fracability and clean fracture faces to increase permeability and decrease proppant embedment. The reactive gases may be suited for CO₂-based fracturing fluids because unlike conventional oxidizers, the reactive oxidizer gases here are generally soluble in non-polar solvents. The oxidizing gas as molecules may exist as a gas or supercritical fluid (at reservoir conditions) that is soluble in supercritical CO₂ and has a standard redox potential in excess of 1 volt. Reservoir conditions may be, for example, temperature greater than 200 °F and pressure greater than 3000 pounds per square inch gauge (psig). These reactive gases include, for example, bromine (Br₂), chlorine (Cl₂), fluorine (F₂), chlorine monofluoride (ClF), chlorine dioxide (ClO₂), oxygen (O₂), ozone (O₃), nitrous oxide (N₂O), or nitrite (NO₂) gases. Reactive gases may also be generated in situ upon injection of precursors with CO₂ into the formation.

[0084] The technique may involve mixing of supercritical CO₂ with an oxidizing gas stream. These oxidizing gas chemicals can be mixed on-the-fly with liquid CO₂ and surfactant to form the emulsion and pumped. The oxidant (oxidizer) should be consumed downhole and therefore may beneficially preclude flowback treatment or disposal. If the oxidant is prepared in situ, then the precursors may be injected with supercritical CO₂. For example: (1) the first precursor with CO₂ is injected, (2) a CO₂ spacer is then pumped, and (3) the second precursor with CO₂ is then injected. This sequence may prevent or reduce premature reaction of the precursors to form the reactive gas.

[0085] For bromine as the reactive gas, the bromine reacts with the kerogen and pyrite. The bromine may partially depolymerize the kerogen (a geopolymer). This reaction of bromine with kerogen may form light-chain

products that escape when the CO₂ is vented. This reaction of bromine with kerogen may also form a brominated kerogen tar at least partially soluble in CO₂. This kerogen tar may be soluble in hydrocarbons and therefore leave the rock matrix migrating from the formation to the wellbore.

5 **[0086]** As for supply of ClO₂ as an oxidizer in the supercritical CO₂, ClO₂ generators commercially available may be deployed at the well site. The ClO₂ gas can be mixed with liquid CO₂ on-the-fly for the stimulation and treatment of organic-rich shale formation for enhanced hydrocarbon production. The ClO₂ gas generally does not hydrolyze when entering water and remains a
10 dissolved gas in solution. The ClO₂ gas may be up to 10 times more soluble in water than is chlorine and therefore a larger dose (compared to chlorine) of the oxidizer gas ClO₂ can be delivered to the formation. In lieu of relying on ClO₂ generators, the ClO₂ gas may instead be generated in situ (downhole in the wellbore) via, for example, utilizing sodium chlorite. Over time, produced ClO₂
15 gas may help degrade the kerogen and increase production. If ClO₂ is the oxidant, ClO₂ should be prepared on site and used as a mixture with air.

[0087] Lastly, other CO₂-based hydraulic fracturing fluids may be employed in tandem with the present reactive VES-based fracturing fluid. For example, CO₂-based fluids with an oxidizer contain in-situ forming halogens may be
20 employed.

[0088] FIG. 10 is a method 1000 of hydraulic fracturing a geological formation. The geological formation includes organic material, such as kerogen.

[0089] At block 1002, the method includes providing a VES fracturing fluid
25 having a surfactant and an inorganic oxidizer salt through a wellbore into the geological formation. In implementations, the method includes pumping the VES fracturing fluid through the wellbore into the geological formation. The pumping may inject the VES fracturing fluid through perforations in cemented casing of the wellbore into the geological formation. The VES fracturing fluid
30 may be a reactive VES fracturing fluid because of the presence of the inorganic oxidizing salt in the VES fracturing fluid. The concentration of the

inorganic oxidizing salt in the VES fracturing fluid may be, for example, in a range of 1 wt% to 20 wt%. In some implementations, the concentration of the inorganic salt in the reactive VES fracturing fluid is at least 3 wt% or at least 5 wt%.

5 **[0090]** The VES fracturing fluid may include water. The VES fracturing fluid may include the surfactant at a concentration in a range of 0.1 wt% to 10 wt%. The method may include forming worm-like micelles from molecules of the surfactant to increase viscosity of the reactive VES fracturing fluid. The reactive VES fracturing fluid may include polymer to further increase viscosity
10 of the reactive VES fracturing fluid. In other embodiments, the VES fracturing fluid does not include polymer.

[0091] The VES fracturing fluid may include another salt that is a monovalent salt or a divalent salt to promote formation of worm-like micelles from molecules of the surfactant that entangle to increase viscosity of the VES
15 fracturing fluid. The reactive VES fracturing fluid may have this salt (for example, a monovalent salt or a divalent salt) that is not an oxidizer to promote micelle formation of the surfactant and with this salt at a concentration of less than 15 wt% in the VES fracturing fluid.

[0092] The method may include optionally adding proppant to the VES
20 fracturing fluid. The VES fracturing fluid have proppant for at least a portion of time of providing (pumping) the VES fracturing fluid through the wellbore into the geological formation.

[0093] At block 1004 the method includes hydraulically fracturing the geological formation via the providing (pumping) of the VES fracturing fluid to
25 form hydraulic fractures in the geological formation. The organic material (for example, kerogen) is present in the hydraulic fractures. Kerogen exists at fracture faces of the hydraulic fractures. In the initial forming of the hydraulic fractures, the kerogen blocks permeability between portions of the fracture faces and the geological formation. A fracture face is generally an interface of
30 a hydraulic fracture with the geological formation.

[0094] At block 1006, the method includes oxidizing organic material (for example, kerogen) in the hydraulic fractures with the VES fracturing fluid. The oxidizing of the organic material may involve degrading and fragmenting the organic material. The oxidizing of the organic material may make the organic material (or at least a portion of the organic material) soluble in aqueous fluid. The degrading of the organic material may involve fragmenting the organic material to generate a permeable channel through the organic material. The oxidizing may include oxidizing organic material at a fracture face of the hydraulic fracture to fragment the organic material at the fracture face to generate a permeable channel from the geological formation into the hydraulic fracture. The generating the permeable channel increases conductivity of hydrocarbon from the geological formation through the hydraulic fracture to the wellbore. While fragments of the organic material may remain at the fracture face, the permeability is increased due the oxidation and attack by the VES fracturing fluid having the inorganic oxidizer salt. The oxidizing may include degrading the organic material involving dividing the organic material into pieces that can be solubilized in aqueous treatment fluid that is flowed back through the wellbore to the Earth surface.

[0095] At block 1008, the method includes specifying a concentration of the inorganic oxidizer salt in a VES fracturing fluid. The method may include specifying a concentration of the inorganic oxidizer salt in the VES fracturing fluid (reactive) based at least in part on an amount of kerogen in the geological formation. The VES fracturing fluid may include the inorganic oxidizer salt at the concentration as specified. The method may include adding the inorganic oxidizer salt to the reactive VES fracturing fluid to give the concentration as specified.

[0096] The concentration of the inorganic oxidizer salt in the VES fracturing fluid can depend on the quantity of kerogen or other organic matter in the reservoir rock in the geological formation, such as in the region of the geological formation being subjected to hydraulic fracturing with the VES fracturing fluid. The concentration of the inorganic oxidizer salt in the VES

fracturing fluid to implement can be determined (specified) based on the particular inorganic oxidizer salt selected and on the amount and type of kerogen in the geological formation. Source-rock samples collected from the geological formation being hydraulically fractured or to be hydraulically fractured can be collected and analyzed. For example, laboratory tests (for instance, including etching) can be performed on kerogen embedded in rock surfaces of the samples. Further, the weight percent of the total organic carbon (TOC) in the formation can be determined, for example, via a TOC analyzer or pyrolysis unit. The amount of kerogen in the subterranean region of the geological formation to be hydraulically fractured can be calculated, determined, or estimated.

[0097] The amount of pyrite or other iron sulfides in the subterranean formation may also be considered in specifying the concentration of the inorganic oxidizer salt in the VES fracturing fluid. The weight percent of iron sulfide in the formation can be determined, for example, by testing the source-rock samples employing x-ray fluorescence, x-ray diffraction, or energy dispersive x-ray spectroscopy. The amount of kerogen or iron sulfide can also be taken, deduced, or inferred from well logs in certain instances. The determining or specifying the inorganic oxidizer salt concentration can account for the amount of inorganic oxidizer salt needed to degrade the organic material including kerogen while also accounting for the iron sulfide present in the formation.

[0098] The rock surface area within the fracture network that the reactive VES fluid will make contact in the formation can be considered with respect to specifying concentration of the inorganic oxidizer salt in the VES fluid. The expected size of the fracture network and the resulting surface area of the fractured zones can be estimated. Other factors relevant in determining or calculating the amount (concentration) of inorganic oxidizer salt to specify in the reactive VES fluid may include: (1) any organic components in the VES fluid; and (2) any organic components and amount of fluid downhole (including

in the wellbore) at the time of placing the reactive VES fluid through the wellbore into the geological formation.

[0099] At block 1010, the method optionally includes alternating or sequencing the reactive VES fracturing fluid. The VES-based fluid containing oxidative materials and proppant may be pumped alternatively with VES-based fluid containing oxidative materials and no proppant as a hybrid treatment. The VES-based fracturing fluid may also be pumped as part of conductivity channel fracturing. In other applications, the method may include providing (pumping) a slickwater fracturing fluid through the wellbore into the geological formation before (and after) providing the VES fracturing fluid through the wellbore into the geological formation. The slickwater fracturing fluid may include an oxidizer. The VES fracturing fluid may include proppant. The method may include pumping a slickwater fracturing fluid through the wellbore into the geological formation in sequence with the pumping of the reactive VES-based fracturing fluid, where the VES-based fracturing fluid has proppant.

[0100] The method may include a sequence that alternates pumping a CO₂-based fracturing fluid with pumping the VES fracturing fluid having the oxidizer. The method may include alternating in a sequence: (1) providing a CO₂-based fracturing fluid through the wellbore into the geological formation with (2) providing the VES fracturing fluid through the wellbore into the geological formation. The CO₂-based fracturing fluid may have an oxidizer to attack kerogen.

[0101] At block 1012, the method may further include in addition to hydraulic fracturing, the production of hydrocarbon from the geological formation. The method may include producing hydrocarbon from the geological formation through the permeable channel (block 1006) and the hydraulic fracture(s) to the wellbore.

[0102] At block 1014, the method may include applying a reactive VES fluid for treatments other than hydraulic fracturing. This reactive VES-based treatment fluid may be the same or similar as the aforementioned VES fracturing fluid applied for hydraulic fracturing. These additional treatments

may be outside of the context of hydraulic fracturing or in combination with the hydraulic fracturing. Implementations of treatments with the VES-based treatment fluid include: (1) upgrading oil in the subterranean formation (geological formation) by oxidizing the oil to reduce the boiling point of the oil; 5 (2) degrading filter cake during open hole drilling or during hydraulic fracturing; (3) breaking organic matter (for example, paraffin, bitumen, or oil) in the subterranean formation by reducing the viscosity of the organic matter; and (4) removing organic scale (buildup) from a subterranean formation for clean-up to facilitate subsequent fluid injection for the wellbore employed as an injection 10 well. The inorganic oxidizer salt in the VES treatment fluid may include iodates (IO_3^-).

[0103] Iodate salts may be included as the inorganic oxidizer salt in the VES fluid for options of heavy oil upgrading, in situ methane conversion, and other applications. The iodate salt may be IO_3^- paired with lithium, sodium, 15 potassium, magnesium, etc.

[0104] An implementation may be to pump the present VES fluid (having an inorganic oxidizer salt) through a wellbore into the subterranean formation to upgrade heavy oil in the subterranean formation. The upgrade of the heavy oil may be performed with the wellbore as an open hole wellbore. Heavy oil can 20 include asphalt and bitumen. Heavy oil may be crude oil having an API gravity less than 22° , less than 21° , or less than 20° . Heavy oil may be crude oil having an API gravity in the range of 10° to 22° , 10° to 21° , or 10° to 20° . Crude oil with an API gravity less than 10° can be characterized or labeled as extra-heavy crude oil. The VES fluid (VES-based fluid) can be employed to 25 upgrade heavy oil or extra-heavy oil. The upgrade may be to reduce the boiling point and viscosity of the heavy oil. The oxidization of the heavy oil by the VES fluid may degrade the heavy oil. The degradation may upgrade the heavy oil in the sense of reducing the boiling point and viscosity. The oxidation may dissolve resinous components of the heavy oil. The oxidation 30 may reduce the molecular weight of the heavy oil by breaking molecular chains

(molecules) of the heavy oil into shorter chains (molecules) and thus reduce the viscosity and boiling point of the heavy oil.

[0105] Another implementation is to pump the present reactive VES fluid (reactive VES-based fluid) through a wellbore into the subterranean formation to degrade and remove filter cake. A property of drilling fluid (mud) may be the formation of a filter cake. This filter cake may be deposited on the porous rocks under overbalance pressure conditions. Filter cake (mud cake or wall cake) may be a layer formed by solid particles in drilling mud against porous zones due to differential pressure between hydrostatic pressure and formation pressure. The structure of the filter cake may include a solid deposition insoluble in water. The material insoluble in water may be organic material. The removal of the filter cake with the present VES fluid may be in open hole drilling or during hydraulic fracturing. The VES fluid may oxidize (attack) the filter cake to break down and dissolve (or dislodge) the filter cake. The oxidizing of organic material with the reactive VES fluid may involve degrading a filter cake with the reactive VES fluid during drilling of the wellbore as an open hole wellbore or during hydraulic fracturing of the subterranean (geological) formation.

[0106] Other implementations include to pump the reactive VES fluid (reactive VES-based fluid) through a wellbore into a subterranean formation to break organic matter (for example, paraffin, bitumen, or oil) in the subterranean formation. The breaking (reducing the viscosity) of the organic matter may be by oxidation via the VES fluid. The oxidation may dissolve or partially dissolve the organic matter to reduce viscosity. Such may advance formation conductivity and thus subsequent oil and gas production. Yet other implementations may pump the present VES through a wellbore of an injection well to remove organic scale (buildup, residue) from a subterranean formation for clean-up of the organic scale. Such may facilitate subsequent fluid injection through the wellbore and subterranean formation in the operation of the injection well.

Examples

[0107] The Example are given only as examples and not meant to limit the present techniques. Example 1 and Example 2 are presented.

Example 1

[0108] Example 1 is directed to evaluating substitution of sodium bromate (an inorganic oxidizer salt) for typical salt in a VES fluid. In particular, three VES-based fluids were prepared in order to determine the effect of adding strong oxidizing salts (sodium bromate in particular in Example 1) to the fluid mixture and whether an oxidizing salt could replace the calcium chloride (or potassium chloride) typically used in VES fluids for hydraulic fracturing applications. The three VES fluids were prepared with water and erucamidopropyl hydroxypropylsultaine (as the viscoelastic surfactant) commercially known as Armovis EHS[®] available from Akzo Nobel N.V. having headquarters in Amsterdam, Netherlands. Salt was added to the three VES fluids. In particular the three VES fluids included: (1) the VES fluid containing calcium chloride (CaCl_2) salt; (2) the VES fluid containing both CaCl_2 salt and sodium bromate (NaBrO_3) oxidizer salt; and (3) the VES fluid containing NaBrO_3 oxidizer salt.

[0109] FIG. 11 is Table 1 (1100) giving solution parameters for these three VES fluid samples prepared for viscosity measurements. The sample column 1102 notes the respective sample number of 1, 2, or 3. The water 1104 in each sample was 135 milliliters (mL). The VES 1106 (erucamidopropyl hydroxypropylsultaine) in each sample was 7.5 mL. The amount 1108 of calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) is given in grams (g). The molality (m) 1110 of CaCl_2 is given in kilogram per mole of solution of the respective VES fluid samples. The amount 1112 of NaBrO_3 is given in grams (g). The molality (m) 1114 of NaBrO_3 is given in kilogram per mole of solution of the respective VES fluid samples. The total ion molality 1116 is give in kilograms per mole of solution of the respective VES fluid samples. The three samples of the VES fluids were prepared by first dissolving the salt(s) in the volume of water 1104 listed in the table. Then, the VES 1108 was added and the solution agitated for mixing.

[0110] After each fluid was prepared, the viscosity was measured with a rheometer. The temperature was initially ramped to 200 °F and held until the viscosity stabilized. The viscosity of all three fluids were similar (around 200 cP) with the most viscosity (about 230 cP) corresponding to the most total ion molality in solution and the least viscosity (about 175 cP) corresponding to the least total ion molality in solution. The effect of oxidizing salt as a replacement or addition is beneficially negligible, which suggests that the charge added by this salt is sufficient to encourage worm-like micelle formation in solution. This evaluation also shows that the surfactant is not susceptible to oxidative degradation at these temperatures. These two factors demonstrate that this fluid could be effectively pumped into the unconventional source rock formation.

[0111] In the tests, the temperature of the fluids were ramped and held to a series of greater temperatures: 250 °F, 300 °F, and 350 °F. At 250 °F, the viscosities of the fluids notably drop to about 100 cP, but the viscosities are stable at that temperature suggesting that the fluids had not degraded. Further temperature ramping (through 300 °F to 350 °F) shows the viscosity dropping to about 0 cP. These temperatures of 300+ °F, however, are beyond the temperatures at which these fluids are pumped and therefore do not limit application of the fluids.

[0112] FIG. 12 is a plot 1200 of viscosity (cP) 1202 and temperature (°F) 1204 over time 1206 in hours (h). The plot 1200 gives rheological data for the three samples of VES-based fluid. The curve 1208 is the viscosity of sample 1. The curve 1210 is the viscosity of sample 2. The curve 1212 is the viscosity of sample 3. The three curves 1214 for temperature of the three samples, respectively, are essentially same at the relevant portion (temperatures) of the tests.

Example 2

[0113] Example 2 is directed to evaluating stability of a VES-based fluid having an inorganic oxidizer salt and a polymer. A polymer may be added to a VES fluid to boost viscosity of the VES fluid. However, the polymer may be

susceptible to oxidative degradation. To evaluate whether such degradation would occur at the temperatures and timescale of a hydraulic fracturing job with a reactive VES, a VES fluid containing sodium bromate (an inorganic oxidizer salt) as the sole salt was prepared with three different amounts of a polymer. The polymer was Flopaam™ 5915 SH (abbreviated here as FP5915SH) from SNF Floerger having headquarters in Andrézieux, France. The FP5915SH polymer is a hydrophobically modified anionic-polyacrylamide-based terpolymer with the hydrophobic monomer content less than 1.5 mol % and containing 10-25 mol % of sulfonic monomer. The FP5915SH polymer was added in slurry form to three VES fluid samples.

[0114] FIG. 13 is Table 2 (1300) giving components of the tested fluids (the three VES fluid samples). Table 2 are solution parameters for the three VES fluids prepared with polymer additive FP9515SH for viscosity measurement. The sample column 1302 notes the respective sample number of 4, 5, or 6. The water 1304 in each sample was 135 mL. The VES 1306 (erucamidopropyl hydroxypropylsultaine) in each sample was 7.5 mL. The volume 1308 of FP9515SH polymer slurry added is given in mL. The amount 1310 of NaBrO₃ is given in grams (g). The molality (m) 1312 of NaBrO₃ is given in kilogram per mole of solution of the respective VES fluid samples.

[0115] FIG. 14 is a plot 1400 of viscosity (cP) 1402 and temperature (°F) 1404 over time 1406 in hours (h). The plot 1400 gives rheological data for the three samples of VES-based fluid prepared with the FP9515SH polymer. Fluid compositional data is given in Table 2 of FIG. 13. In FIG. 14, the curve 1408 is the viscosity of sample 4. The curve 1410 is the viscosity of sample 5. The curve 1412 is the viscosity of sample 6. The curves 1414 is the approximate temperature of the three samples 4, 5, and 6 during the viscosity during the viscosity measurements. As can be seen in plot 1400, increasing addition of the polyacrylamide terpolymer (FP9515SH) increases the viscosity of the VES fluid. The fluid is stable at 200 °F.

[0116] An embodiment is a method of hydraulic fracturing, including providing a VES fracturing fluid having a surfactant and an inorganic oxidizer

salt through a wellbore into a geological formation to hydraulically fracture the geological formation to form a hydraulic fracture in the geological formation. The method includes oxidizing organic material in the hydraulic fracture with the VES fracturing fluid. The oxidizing of the organic material includes
5 degrading (for example, fragmenting) the organic material, which includes kerogen. The oxidizing of the organic material may make at least a portion of the organic material soluble in aqueous fluid. The degrading of the organic material may involve fragmenting the organic material to generate a permeable channel through the organic material. The oxidizing may include oxidizing
10 organic material at a fracture face of the hydraulic fracture to fragment the organic material at the fracture face to generate a permeable channel from the geological formation into the hydraulic fracture to increase conductivity of hydrocarbon from the geological formation through the hydraulic fracture to the wellbore. The fracture face may be an interface of the hydraulic fracture with
15 the geological formation.

[0117] In certain implementations, the VES fracturing fluid does not include polymer. The concentration of the surfactant in the VES fracturing fluid may be in a range of 0.1 wt% to 10 wt%. The method may include specifying a concentration of the inorganic oxidizer salt in the VES fracturing fluid based at
20 least in part on an amount of kerogen in the geological formation. The VES fracturing fluid may have the inorganic oxidizer salt at the concentration as specified. The concentration of the inorganic salt in the VES fracturing fluid may be in a range of 1 wt% to 20 wt%. The inorganic oxidizer salt may include LiClO_3 , NaClO_3 , KClO_3 , $\text{Mg}(\text{ClO}_3)_2$, $\text{Ca}(\text{ClO}_3)_2$, $\text{Sr}(\text{ClO}_3)_2$, $\text{Ba}(\text{ClO}_3)_2$, LiBrO_3 ,
25 NaBrO_3 , KBrO_3 , $\text{Mg}(\text{BrO}_3)_2$, $\text{Ca}(\text{BrO}_3)_2$, $\text{Sr}(\text{BrO}_3)_2$, or $\text{Ba}(\text{BrO}_3)_2$, or any combinations thereof. The inorganic oxidizer salt may include iodates (IO_3^-).

[0118] Iodate salts may be including as the inorganic oxidizer salt with the present VES as a delivery method, for example, for options of heavy oil upgrading, in situ methane conversion, and other applications. The specific
30 iodate (IO_3^-) salt may be similar salts to the aforementioned salts with lithium, sodium, potassium, magnesium, etc.

[0119] The VES fracturing fluid may have another salt (in addition to the inorganic oxidizer salt) that is a monovalent salt or a divalent salt to promote formation of worm-like micelles from molecules of the surfactant that entangle to increase viscosity of the VES fracturing fluid. The other salt may include
5 LiF, NaF, KF, MgF₂, CaF₂, SrF₂, BaF₂, LiCl, NaCl, KCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, LiBr, NaBr, KBr, MgBr₂, CaBr₂, SrBr₂, or BaBr₂, or any combinations thereof.

[0120] The method may include adding proppant to the VES fracturing fluid. The VES fracturing fluid may include the proppant for at least a portion of time
10 of providing the VES fracturing fluid through the wellbore into the geological formation. The method may include providing a slickwater fracturing fluid (for example, also having an oxidizer) through the wellbore into the geological formation before or after providing the VES fracturing fluid through the wellbore into the geological formation. The method may include providing a viscosified
15 fracturing fluid through the wellbore into the geological formation before or after providing the VES fracturing fluid through the wellbore into the geological formation. The method may include providing a CO₂-based fracturing fluid through the wellbore into the geological formation before or after providing the VES fracturing fluid through the wellbore into the geological formation. The
20 CO₂-based fracturing fluid may have an organic oxidizer that attacks the organic material. The CO₂-based fracturing fluid includes a reactive gas that attacks the organic material. The reactive gas may be, for example, Br₂, Cl₂, F₂, ClF, ClO₂, O₂, O₃, N₂O, or NO₂, or any combinations thereof.

[0121] Another embodiment is a method including pumping a reactive VES
25 fracturing fluid having a surfactant and an inorganic oxidizer salt through a wellbore into a geological formation for hydraulic fracturing of the geological formation. The method includes forming hydraulic fractures in the geological formation with the reactive VES fracturing fluid and oxidizing organic material in the hydraulic fractures with the reactive VES fracturing fluid. The method
30 includes generating a permeable channel through organic material at a fracture face of a hydraulic fracture between the geological formation and the

hydraulic fracture via oxidizing of the organic material at the fracture face with the reactive VES fracturing fluid. The oxidizing of the organic material (for example, including kerogen) at the fracture face may fragment the organic material at the fracture face. In certain implementations, the concentration of the inorganic salt in the reactive VES fracturing fluid is at least 3 wt%. In some implementations, the inorganic oxidizer salt may include magnesium peroxide, calcium peroxide, sodium nitrate, sodium nitrite, sodium persulfate, potassium persulfate, sodium tetraborate, sodium percarbonate, sodium hypochlorite, an iodate salt, a periodate salt, a dichromate salt, or a permanganate salt, or any combinations thereof. The oxidizing may include degrading the organic material involving dividing the organic material into pieces that can be solubilized in aqueous treatment fluid that is flowed back through the wellbore to the Earth surface.

[0122] The method may include forming worm-like micelles from molecules of the surfactant to increase viscosity of the reactive VES fracturing fluid. The reactive VES fracturing fluid may further include polymer to further increase viscosity of the reactive VES fracturing fluid. The reactive VES fracturing fluid may include a salt that is not an oxidizer to promote micelle formation of the surfactant. This salt may be, for example, a monovalent salt or a divalent salt and at a concentration in the reactive VES fracturing fluid less than 15 wt%. The method may include specifying a concentration of the inorganic oxidizer salt in the reactive VES fracturing fluid based at least in part on an amount of kerogen in the geological formation. The method may include adding the inorganic oxidizer salt to the reactive VES fracturing fluid to give the concentration as specified. The reactive VES fracturing fluid may include proppant for at least a portion of time of pumping the reactive VES fracturing fluid through the wellbore into the geological formation. The method may include pumping a slickwater fracturing fluid through the wellbore into the geological formation in sequence with the pumping of the reactive VES-based fracturing fluid having proppant in the sequence. The method may include

producing hydrocarbon from the geological formation through the permeable channel and the hydraulic fracture to the wellbore.

[0123] Yet another embodiment is a reactive VES fracturing fluid for hydraulic fracturing of a geological formation. The reactive VES fracturing fluid includes a surfactant at a concentration in the reactive VES fracturing fluid in a range of 0.1 wt% to 10 wt%. The reactive VES fracturing fluid includes an inorganic oxidizer salt for the reactive VES fracturing fluid to degrade kerogen in the geological formation. The concentration of the inorganic oxidizer salt in the VES fracturing fluid may be in a range of 1 wt% to 20 wt%. The concentration of the inorganic oxidizer salt in the VES fracturing fluid may be at least 3 wt%. In implementations, the inorganic oxidizer salt may promote micelle formation of the surfactant. The inorganic oxidizer salt may include LiClO_3 , NaClO_3 , KClO_3 , $\text{Mg}(\text{ClO}_3)_2$, $\text{Ca}(\text{ClO}_3)_2$, $\text{Sr}(\text{ClO}_3)_2$, $\text{Ba}(\text{ClO}_3)_2$, LiBrO_3 , NaBrO_3 , KBrO_3 , $\text{Mg}(\text{BrO}_3)_2$, $\text{Ca}(\text{BrO}_3)_2$, $\text{Sr}(\text{BrO}_3)_2$, or $\text{Ba}(\text{BrO}_3)_2$, or any combinations thereof. The inorganic oxidizer salt may include magnesium peroxide, calcium peroxide, sodium nitrate, sodium nitrite, sodium persulfate, potassium persulfate, sodium tetraborate, sodium percarbonate, sodium hypochlorite, an iodate salt, a periodate salt, a dichromate salt, or a permanganate salt, or any combinations thereof. The reactive VES fracturing fluid may include a salt that is not the inorganic oxidizer salt, that is inert to oxidation, and that promotes micelle formation of the surfactant to increase viscosity of the reactive VES fracturing fluid. Concentration of this salt (for example, a monovalent salt or a divalent salt) in the reactive VES fracturing fluid is generally in a range of 1 wt% to 50 wt%, or may be less than 15 wt%. This salt that is not the inorganic oxidizer salt may include LiF , NaF , KF , MgF_2 , CaF_2 , SrF_2 , BaF_2 , LiCl , NaCl , KCl , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 , LiBr , NaBr , KBr , MgBr_2 , CaBr_2 , SrBr_2 , or BaBr_2 , or any combinations thereof. The reactive VES fracturing fluid may include phthalic acid, salicylic acid, or their salts, or any combination thereof. The reactive VES fracturing fluid may include a crosslinkable polymer. The reactive VES fracturing fluid may include a

crosslinked polymer that increases viscosity of the reactive VES fracturing fluid.

[0124] Yet another embodiment is a reactive VES fracturing fluid for hydraulic fracturing of a subterranean formation. The reactive VES fracturing fluid includes water (for example seawater), a surfactant at a concentration in the reactive VES fracturing fluid in a range of 0.5 wt% to 10 wt%, and an inorganic oxidizer salt for the reactive VES fracturing fluid to oxidize kerogen in the subterranean formation to fragment the kerogen. The VES fracturing fluid may have another salt including a monovalent salt or a divalent salt, or a combination thereof, to promote micelle formation of the surfactant. The surfactant may be a zwitterionic surfactant that is a betaine or a sultaine. The surfactant may be a zwitterionic surfactant that is a dihydroxyl alkyl glycinate, alkyl ampho acetate or propionate, alkyl amidoamine oxide, gemini VES, alkyl betaine, alkyl amidopropyl betaine, alkylimino mono-propionates, or alkylimino di-propionates, or any combinations thereof. The surfactant may be a zwitterionic surfactant that is disodium tallowiminodipropionate, disodium oleamidopropyl betaine, or erucylamidopropyl betaine, or any combinations thereof. The surfactant may be a cationic surfactant, such as an alkylammonium salt. The alkylammonium salt may include oleyl methyl bis(2-hydroxyethyl)ammonium chloride, erucyl bis(2-hydroxyethyl)methylammonium chloride, N,N,N, trimethyl-1-octadecammonium chloride, cetyltrimethylammonium bromide (CTAB), or dimethylene-1,2-bis(dodecyldimethylammonium bromide), or any combinations thereof. The surfactant may include an anionic surfactant, such as at least one of an alkyl sarcosinate or a sulfanate. The surfactant may include a nonionic surfactant, such as an amido amino oxide. In implementations, the surfactant may include a first surfactant that is a cationic surfactant and a second surfactant that is an anionic surfactant.

[0125] Yet another embodiment is a method of applying a reactive VES-based fluid. The method includes providing the reactive VES-based fluid having a surfactant and an inorganic oxidizer salt through a wellbore into a

subterranean formation. The concentration of the inorganic oxidizer salt in the reactive VES-based fluid is in a range of 1 wt% to 20 wt%. In certain implementations, the concentration is at least 3 wt%. The method includes oxidizing organic material in the subterranean formation with the reactive VES-based fluid. In some implementations, a filter cake includes the organic material. If so, the oxidizing of the organic material involves degrading the filter cake with the reactive VES-based fluid and where the wellbore is an open hole wellbore. The oxidizing of organic material may include degrading a filter cake with the reactive VES-based fluid during drilling of the wellbore, where the wellbore includes an open hole wellbore. The oxidizing of organic material may include degrading a filter cake with the reactive VES-based fluid during hydraulic fracturing of the subterranean formation with the reactive VES-based fluid.

[0126] In implementations, an injection well includes the wellbore. In these implementations, the oxidizing of the organic material involves oxidizing accumulated organic material to remove the accumulated organic material (for example, organic scale or organic residue) to promote fluid injection through the injection well into the subterranean formation. In other implementations, the oxidizing of the organic material involves upgrading oil in subterranean formation with the reactive VES-based fluid. The wellbore may be an open hole wellbore. The oil includes heavy oil having an American Petroleum Institute (API) gravity less than 20°. In implementations, the oxidizing of the organic material comprises breaking organic matter in subterranean formation with the reactive VES-based fluid. The organic matter includes heavy oil or paraffin, or a combination thereof.

[0127] A number of implementations have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the disclosure.

WHAT IS CLAIMED IS:

1. A method of hydraulic fracturing, comprising:
providing a viscoelastic surfactant (VES) fracturing fluid comprising a
5 surfactant and an inorganic oxidizer salt through a wellbore into a geological
formation to hydraulically fracture the geological formation to form a hydraulic
fracture in the geological formation; and
oxidizing organic material in the hydraulic fracture with the VES
fracturing fluid, wherein oxidizing the organic material comprises degrading the
10 organic material, and wherein the organic material comprises kerogen.
2. The method of claim 1, wherein degrading the organic material
comprises fragmenting the organic material.
- 15 3. The method of claim 1, wherein oxidizing comprises oxidizing organic
material at a fracture face of the hydraulic fracture to fragment the organic
material at the fracture face to generate a permeable channel from the
geological formation into the hydraulic fracture to increase conductivity of
hydrocarbon from the geological formation through the hydraulic fracture to the
20 wellbore, wherein the fracture face comprises an interface of the hydraulic
fracture with the geological formation.
4. The method of claim 1, comprising specifying a concentration of the
inorganic oxidizer salt in the VES fracturing fluid based at least in part on an
25 amount of kerogen in the geological formation, wherein the VES fracturing fluid
comprises the inorganic oxidizer salt at the concentration as specified, and
wherein the concentration of the inorganic salt in the VES fracturing fluid is in a
range of 1 weight percent (wt%) to 20 wt%.
- 30 5. The method of claim 1, wherein oxidizing the organic material makes at
least a portion of the organic material soluble in aqueous fluid, and wherein the

inorganic oxidizer salt comprises lithium chlorate (LiClO_3), sodium chlorate (NaClO_3), potassium chlorate (KClO_3), magnesium chlorate [$\text{Mg}(\text{ClO}_3)_2$], calcium chlorate [$\text{Ca}(\text{ClO}_3)_2$], strontium chlorate [$\text{Sr}(\text{ClO}_3)_2$], barium chlorate [$\text{Ba}(\text{ClO}_3)_2$], lithium bromate (LiBrO_3), sodium bromate (NaBrO_3), potassium bromate (KBrO_3), magnesium bromate [$\text{Mg}(\text{BrO}_3)_2$], calcium bromate [$\text{Ca}(\text{BrO}_3)_2$], strontium bromate [$\text{Sr}(\text{BrO}_3)_2$], or barium bromate [$\text{Ba}(\text{BrO}_3)_2$], or any combinations thereof.

6. The method of claim 1, wherein degrading the organic material comprises fragmenting the organic material to generate a permeable channel through the organic material, and wherein the VES fracturing fluid comprises another salt comprising a monovalent salt or a divalent salt to promote formation of worm-like micelles from molecules of the surfactant that entangle to increase viscosity of the VES fracturing fluid.

7. The method of claim 1, wherein the VES fracturing fluid comprises another salt comprising lithium fluoride (LiF), sodium fluoride (NaF), potassium fluoride (KF), magnesium fluoride (MgF_2), calcium fluoride (CaF_2), strontium fluoride (SrF_2), barium fluoride (BaF_2), lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride (MgCl_2), calcium chloride (CaCl_2), strontium chloride (SrCl_2), barium chloride (BaCl_2), lithium bromide (LiBr), sodium bromide (NaBr), potassium bromide (KBr), magnesium bromide (MgBr_2), calcium bromide (CaBr_2), strontium bromide (SrBr_2), or barium bromide (BaBr_2), or any combinations thereof.

8. The method of claim 1, comprising adding proppant to the VES fracturing fluid, wherein the VES fracturing fluid comprises the proppant for at least a portion of time of providing the VES fracturing fluid through the wellbore into the geological formation, wherein the VES fracturing fluid comprises the surfactant at a concentration in a range of 0.1 wt% to 10 wt%, and wherein the VES fracturing fluid does not comprise polymer.

9. The method of claim 1, comprising providing a slickwater fracturing fluid through the wellbore into the geological formation before or after providing the VES fracturing fluid through the wellbore into the geological formation.

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10. The method of claim 9, wherein the slickwater fracturing fluid comprises an oxidizer, and wherein the VES fracturing fluid comprises proppant.

11. The method of claim 1, comprising providing a viscosified fracturing fluid through the wellbore into the geological formation before or after providing the VES fracturing fluid through the wellbore into the geological formation.

12. The method of claim 1, comprising providing a carbon dioxide (CO₂)-based fracturing fluid through the wellbore into the geological formation before or after providing the VES fracturing fluid through the wellbore into the geological formation.

13. The method of claim 12, wherein the CO₂-based fracturing fluid comprises an organic oxidizer that attacks the organic material.

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14. The method of claim 12, wherein the CO₂-based fracturing fluid comprises a reactive gas that attacks the organic material, wherein the reactive gas comprises bromine (Br₂), chlorine (Cl₂), fluorine (F₂), chlorine monofluoride (ClF), chlorine dioxide (ClO₂), oxygen (O₂), ozone (O₃), nitrous oxide (N₂O), or nitrite (NO₂), or any combinations thereof.

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15. A method comprising:

pumping a reactive viscoelastic-surfactant (VES) fracturing fluid comprising a surfactant and an inorganic oxidizer salt through a wellbore into a geological formation for hydraulic fracturing of the geological formation;

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forming hydraulic fractures in the geological formation with the reactive VES fracturing fluid;

oxidizing organic material in the hydraulic fractures with the reactive VES fracturing fluid; and

5 generating a permeable channel through organic material at a fracture face of a hydraulic fracture between the geological formation and the hydraulic fracture via oxidizing of the organic material at the fracture face with the reactive VES fracturing fluid.

10 16. The method of claim 15, comprising forming worm-like micelles from molecules of the surfactant to increase viscosity of the reactive VES fracturing fluid, wherein oxidizing comprises degrading the organic material comprising dividing the organic material into pieces that can be solubilized in aqueous treatment fluid that is flowed back through the wellbore to an Earth surface.

15 17. The method of claim 16, wherein the reactive VES fracturing fluid comprises polymer to further increase viscosity of the reactive VES fracturing fluid.

20 18. The method of claim 15, wherein the reactive VES fracturing fluid comprises a salt that is not an oxidizer to promote micelle formation of the surfactant, the salt comprising a monovalent salt or a divalent salt, and wherein concentration of the salt is less than 15 weight percent (wt%).

25 19. The method of claim 15, wherein oxidizing the organic material at the fracture face fragments the organic material at the fracture face, and wherein the organic material at the fracture face comprises kerogen.

30 20. The method of claim 15, comprising specifying a concentration of the inorganic oxidizer salt in the reactive VES fracturing fluid based at least in part on an amount of kerogen in the geological formation.

21. The method of claim 20, comprising adding the inorganic oxidizer salt to the reactive VES fracturing fluid to give the concentration as specified.

5 22. The method of claim 15, wherein concentration of the inorganic salt in the reactive VES fracturing fluid is at least 3 wt%, and wherein the reactive VES fracturing fluid comprises proppant for at least a portion of time of pumping the reactive VES fracturing fluid through the wellbore into the geological formation.

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23. The method of claim 15, wherein the inorganic oxidizer salt comprises magnesium peroxide, calcium peroxide, sodium nitrate, sodium nitrite, sodium persulfate, potassium persulfate, sodium tetraborate, sodium percarbonate, sodium hypochlorite, an iodate salt, a periodate salt, a dichromate salt, or a
15 permanganate salt, or any combinations thereof.

24. The method of claim 15, comprising pumping a slickwater fracturing fluid through the wellbore into the geological formation in sequence with the pumping of the reactive VES-based fracturing fluid, wherein the VES-based
20 fracturing fluid comprises proppant.

25. The method of claim 15, comprising producing hydrocarbon from the geological formation through the permeable channel and the hydraulic fracture to the wellbore.

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26. A reactive viscoelastic surfactant (VES) fracturing fluid for hydraulic fracturing of a geological formation, the reactive VES fracturing fluid comprising:

a surfactant at a concentration in the reactive VES fracturing fluid in a
30 range of 0.1 weight percent (wt%) to 10 wt%; and

an inorganic oxidizer salt for the reactive VES fracturing fluid to degrade kerogen in the geological formation.

27. The reactive VES fracturing fluid of claim 26, wherein concentration of the inorganic oxidizer salt in the VES fracturing fluid is in a range of 1 wt% to 20 wt%.

28. The reactive VES fracturing fluid of claim 26, wherein concentration of the inorganic oxidizer salt in the VES fracturing fluid is at least 3 wt%, and wherein the inorganic oxidizer salt promotes micelle formation of the surfactant.

29. The reactive VES fracturing fluid of claim 26, wherein the inorganic oxidizer salt comprises lithium chlorate (LiClO_3), sodium chlorate (NaClO_3), potassium chlorate (KClO_3), magnesium chlorate [$\text{Mg}(\text{ClO}_3)_2$], calcium chlorate [$\text{Ca}(\text{ClO}_3)_2$], strontium chlorate [$\text{Sr}(\text{ClO}_3)_2$], barium chlorate [$\text{Ba}(\text{ClO}_3)_2$], lithium bromate (LiBrO_3), sodium bromate (NaBrO_3), potassium bromate (KBrO_3), magnesium bromate [$\text{Mg}(\text{BrO}_3)_2$], calcium bromate [$\text{Ca}(\text{BrO}_3)_2$], strontium bromate [$\text{Sr}(\text{BrO}_3)_2$], or barium bromate [$\text{Ba}(\text{BrO}_3)_2$], or any combinations thereof.

30. The reactive VES fracturing fluid of claim 26, wherein the inorganic oxidizer salt comprises magnesium peroxide, calcium peroxide, sodium nitrate, sodium nitrite, sodium persulfate, potassium persulfate, sodium tetraborate, sodium percarbonate, sodium hypochlorite, an iodate salt, a periodate salt, a dichromate salt, or a permanganate salt, or any combinations thereof.

31. The reactive VES fracturing fluid of claim 26, comprising a salt that is not the inorganic oxidizer salt, wherein the salt is inert to oxidation and promotes micelle formation of the surfactant to increase viscosity of the

reactive VES fracturing fluid, and wherein concentration of the salt in the reactive VES fracturing fluid is in a range of 1 wt% to 50 wt%.

32. The reactive VES fracturing fluid of claim 31, wherein the salt comprises
5 a monovalent salt or a divalent salt.

33. The reactive VES fracturing fluid of claim 26, comprising a salt that is not the inorganic oxidizer salt, wherein concentration of the salt in the reactive VES fracturing fluid is less than 15 wt%, and wherein the salt comprises lithium
10 fluoride (LiF), sodium fluoride (NaF), potassium fluoride (KF), magnesium fluoride (MgF₂), calcium fluoride (CaF₂), strontium fluoride (SrF₂), barium fluoride (BaF₂), lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), strontium chloride (SrCl₂), barium chloride (BaCl₂), lithium bromide (LiBr),
15 sodium bromide (NaBr), potassium bromide (KBr), magnesium bromide (MgBr₂), calcium bromide (CaBr₂), strontium bromide (SrBr₂), or barium bromide (BaBr₂), or any combinations thereof.

34. The reactive VES fracturing fluid of claim 26, comprising phthalic acid,
20 salicylic acid, or their salts, or any combination thereof.

35. The reactive VES fracturing fluid of claim 26, comprising a crosslinkable polymer.

25 36. The reactive VES fracturing fluid of claim 26, comprising a crosslinked polymer that increases viscosity of the reactive VES fracturing fluid.

37. A reactive viscoelastic surfactant (VES) fracturing fluid for hydraulic fracturing of a subterranean formation, the reactive VES fracturing fluid
30 comprising:
water;

a surfactant at a concentration in the reactive VES fracturing fluid in a range of 0.5 weight percent (wt%) to 10 wt%; and

an inorganic oxidizer salt for the reactive VES fracturing fluid to oxidize kerogen in the subterranean formation to fragment the kerogen.

5

38. The reactive VES fracturing fluid of claim 37, comprising another salt comprising a monovalent salt or a divalent salt, or a combination thereof, to promote micelle formation of the surfactant.

10

39. The reactive VES fracturing fluid of claim 37, wherein the surfactant comprises a zwitterionic surfactant comprising a betaine or a sultaine.

15

40. The reactive VES fracturing fluid of claim 37, wherein the surfactant comprises a zwitterionic surfactant comprising a dihydroxyl alkyl glycinate, alkyl ampho acetate or propionate, alkyl amidoamine oxide, gemini VES, alkyl betaine, alkyl amidopropyl betaine, alkylimino mono-propionates, or alkylimino di-propionates, or any combinations thereof.

20

41. The reactive VES fracturing fluid of claim 37, wherein the surfactant comprises a zwitterionic surfactant comprising disodium tallowiminodipropionate, disodium oleamidopropyl betaine, or erucylamidopropyl betaine, or any combinations thereof.

25

42. The reactive VES fracturing fluid of claim 37, wherein the surfactant comprises a cationic surfactant.

43. The reactive VES fracturing fluid of claim 42, wherein the cationic surfactant comprises an alkylammonium salt.

30

44. The reactive VES fracturing fluid of claim 43, wherein the alkylammonium salt comprises oleyl methyl bis(2-hydroxyethyl)ammonium

chloride, erucyl bis(2-hydroxyethyl)methylammonium chloride, N,N,N,trimethyl-1-octadecammonium chloride, cetyltrimethylammonium bromide (CTAB), or dimethylene-1,2-bis(dodecyldimethylammonium bromide), or any combinations thereof.

5

45. The reactive VES fracturing fluid of claim 37, wherein the surfactant comprises an anionic surfactant.

46. The reactive VES fracturing fluid of claim 45, wherein the anionic
10 surfactant comprises at least one of an alkyl sarcosinate or a sulfanate.

47. The reactive VES fracturing fluid of claim 37, wherein the surfactant comprises a nonionic surfactant.

15 48. The reactive VES fracturing fluid of claim 47, wherein the nonionic surfactant comprises an amido amino oxide.

49. The reactive VES fracturing fluid of claim 37, wherein the surfactant
comprises a first surfactant comprising a cationic surfactant and a second
20 surfactant comprising an anionic surfactant.

50. The reactive VES fracturing fluid of claim 37, wherein the water comprises seawater.

25 51. A method of applying a reactive viscoelastic surfactant (VES) based fluid, comprising:

providing the reactive VES-based fluid comprising a surfactant and an inorganic oxidizer salt through a wellbore into a subterranean formation, wherein concentration of the inorganic oxidizer salt in the reactive VES-based
30 fluid is in a range of 1 wt% to 20 wt%; and

oxidizing organic material in the subterranean formation with the reactive VES-based fluid.

52. The method of claim 51, wherein the concentration is at least 3 wt%,
5 wherein oxidizing the organic material comprises degrading a filter cake with the reactive VES-based fluid during drilling of the wellbore, wherein the wellbore comprises an open hole wellbore.

53. The method of claim 51, wherein a filter cake comprises the organic
10 material, and wherein oxidizing the organic material comprises degrading the filter cake with the reactive VES-based fluid, and wherein the wellbore comprises an open hole wellbore.

54. The method of claim 51, wherein oxidizing organic material comprises
15 degrading a filter cake with the reactive VES-based fluid during hydraulic fracturing of the subterranean formation with the reactive VES-based fluid.

55. The method of claim 51, wherein an injection well comprises the wellbore, wherein oxidizing the organic material comprises oxidizing
20 accumulated organic material to remove the accumulated organic material to promote fluid injection through the injection well into the subterranean formation, wherein the accumulated organic material comprises organic scale or organic residue.

25 56. The method of claim 51, wherein oxidizing organic material comprises upgrading oil in subterranean formation with the reactive VES-based fluid, wherein the wellbore comprises an open hole wellbore, and wherein the oil comprises heavy oil comprising an American Petroleum Institute (API) gravity less than 20°.

30

57. The method of claim 51, wherein oxidizing organic material comprises breaking organic matter in subterranean formation with the reactive VES-based fluid, wherein organic matter comprises heavy oil or paraffin, or a combination thereof.

5

58. The method of claim 51, wherein inorganic oxidizer salt comprises an iodate salt.

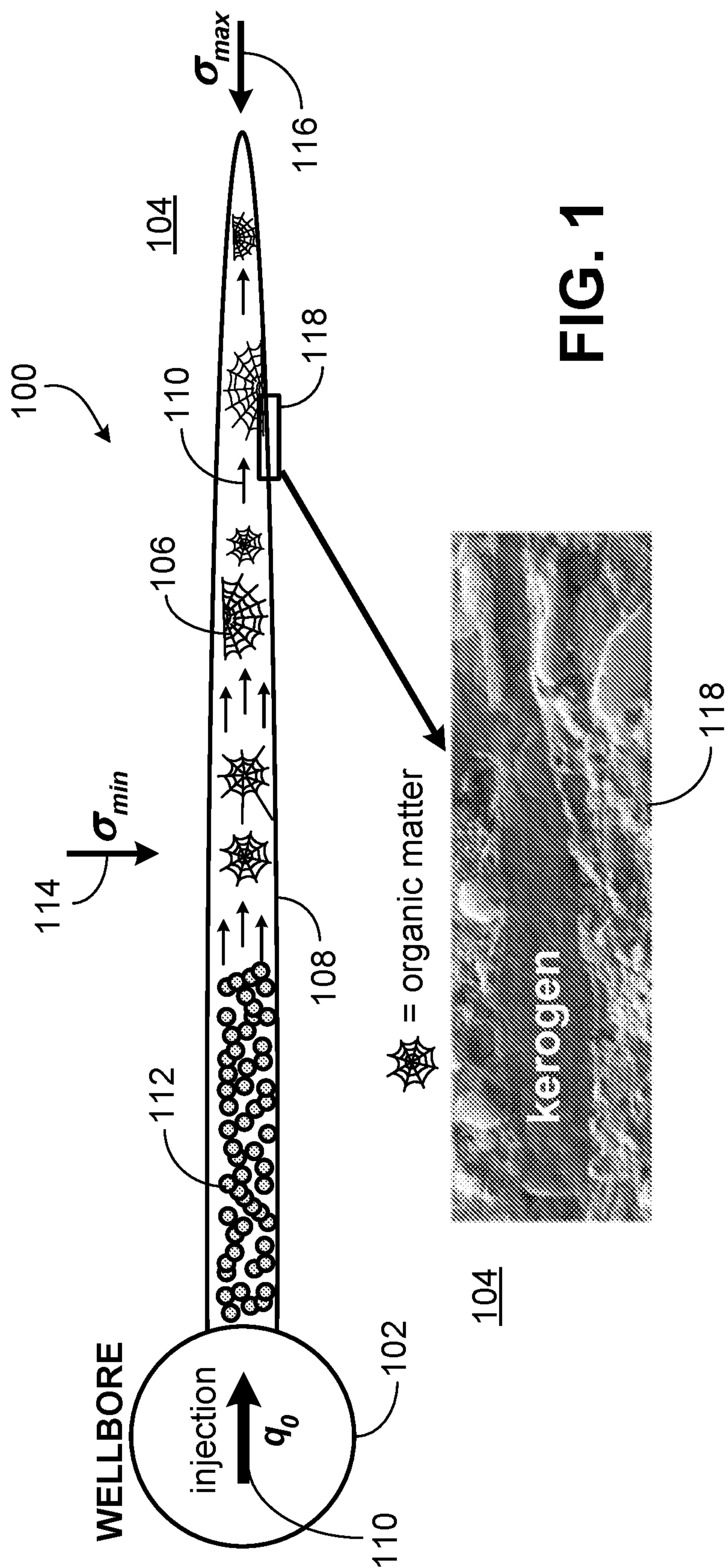


FIG. 1

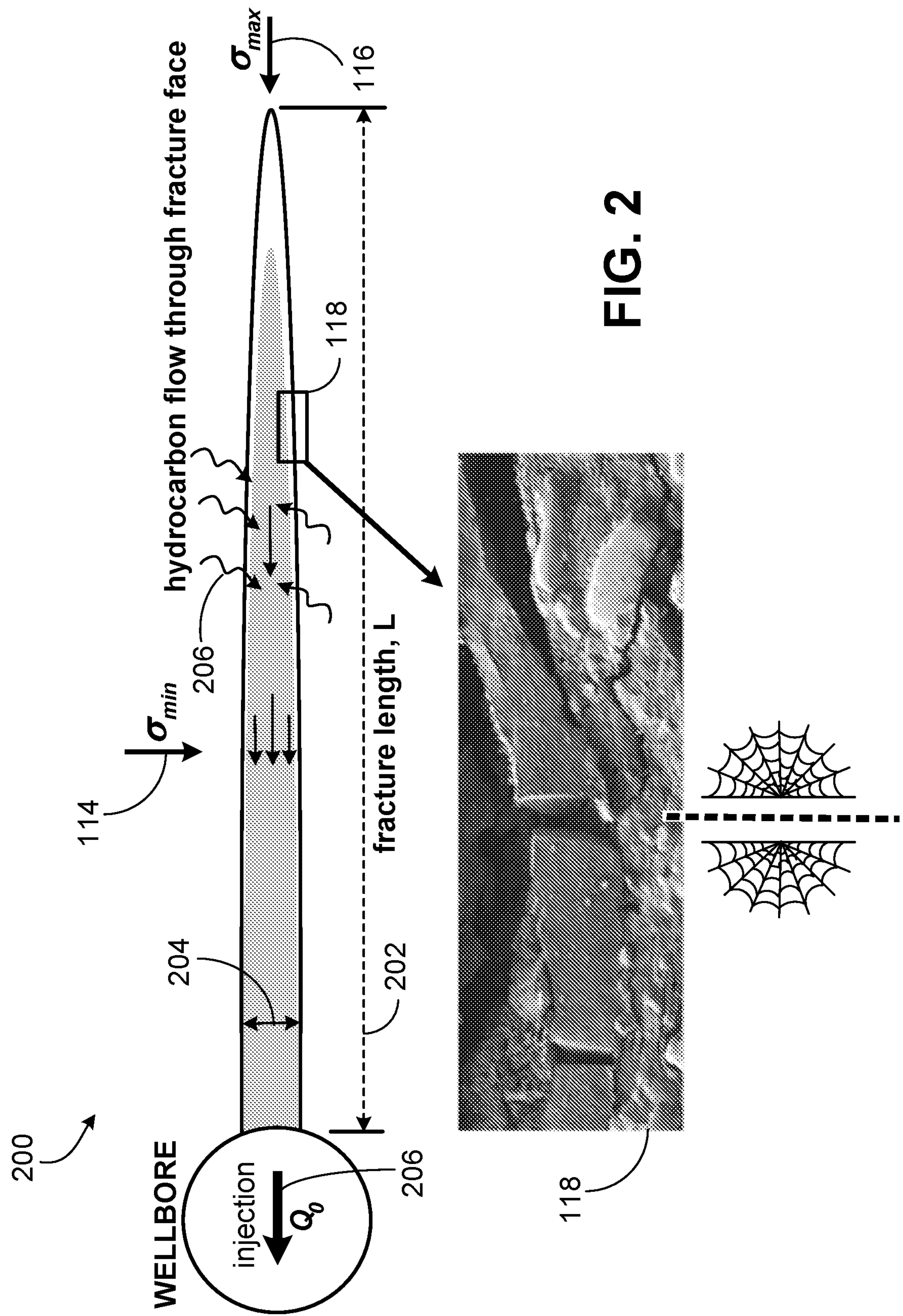


FIG. 2

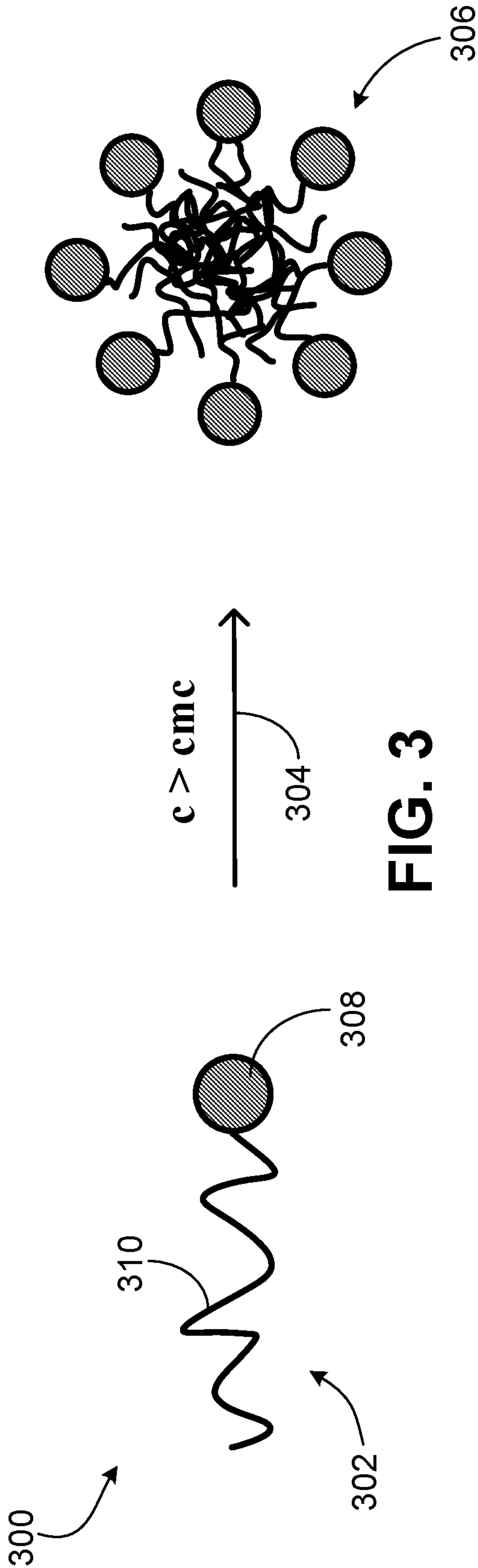


FIG. 3

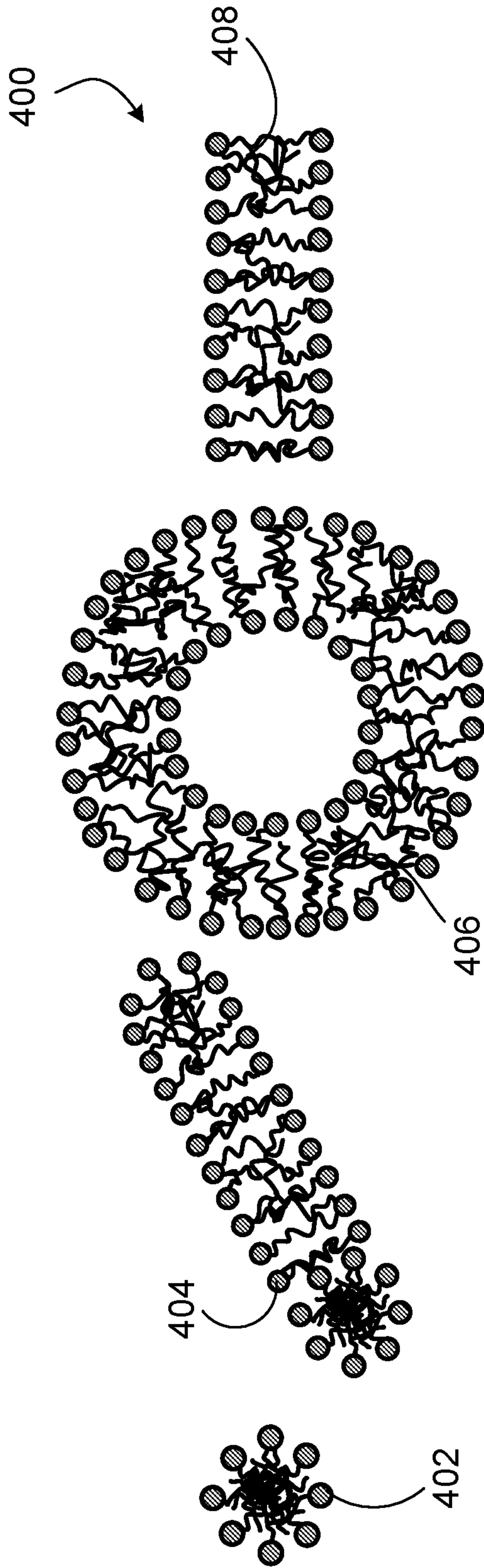


FIG. 4

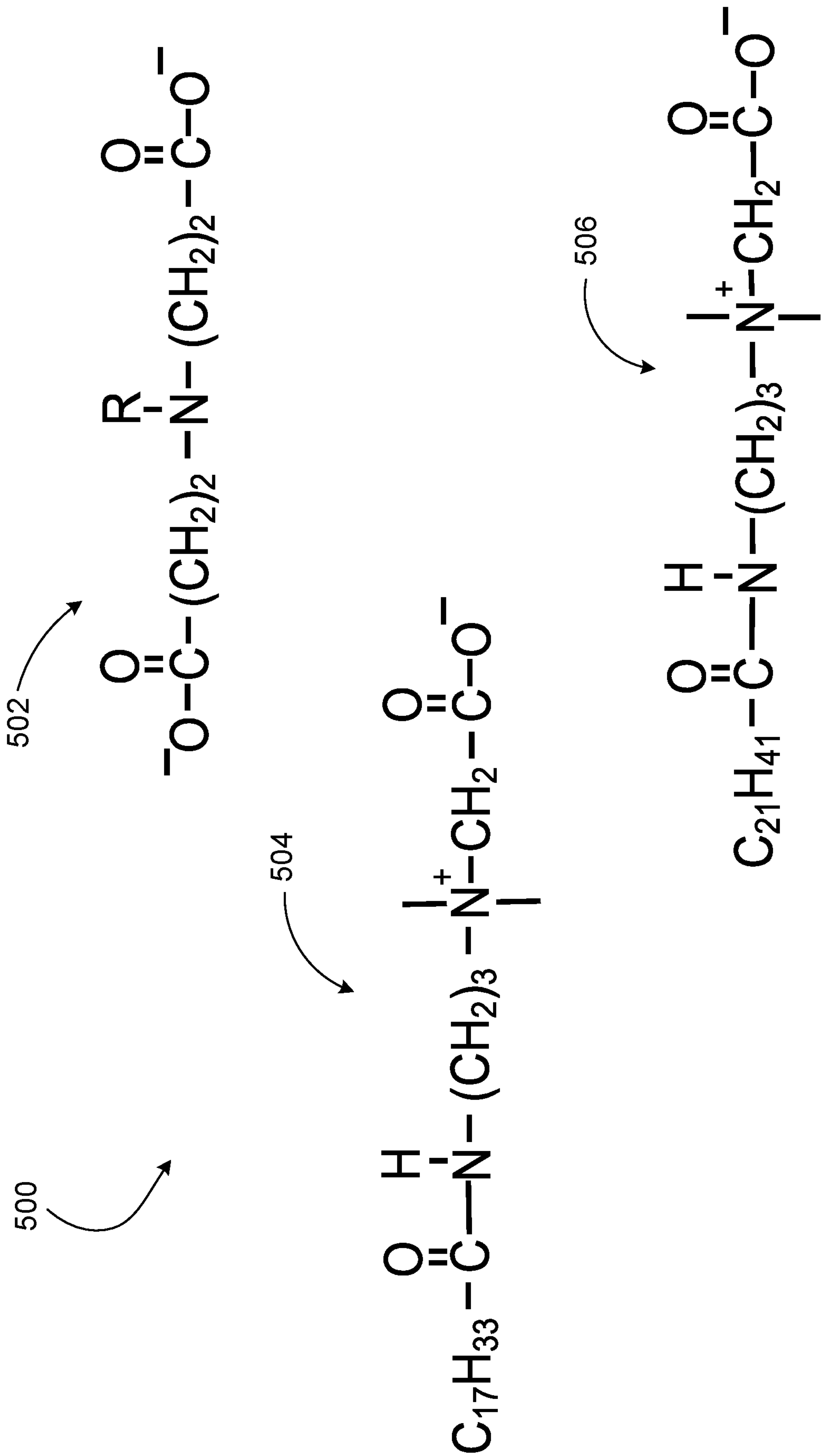


FIG. 5

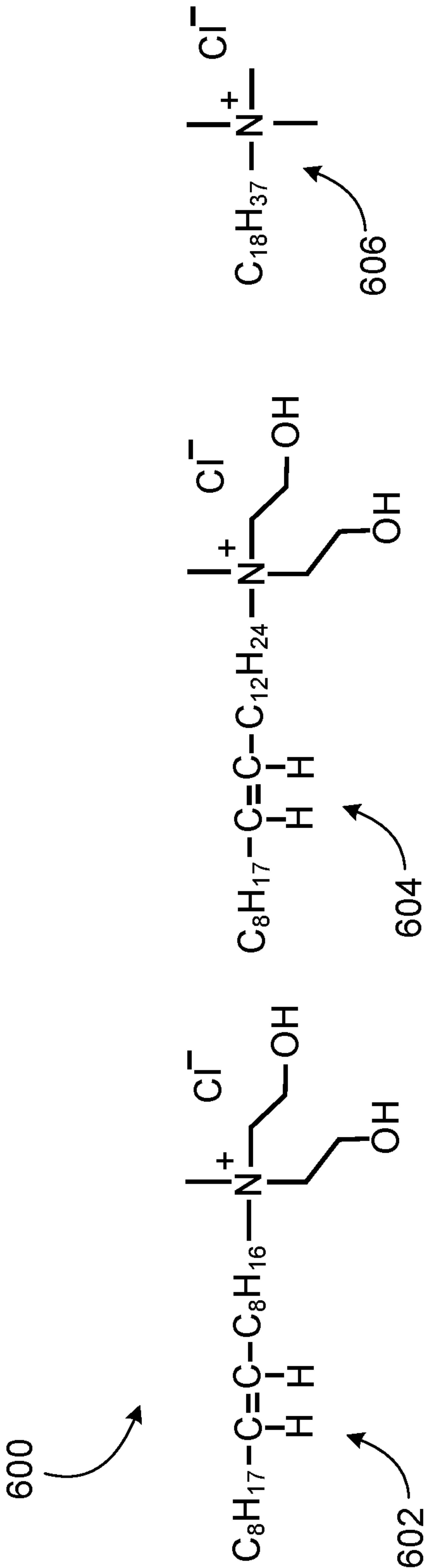


FIG. 6

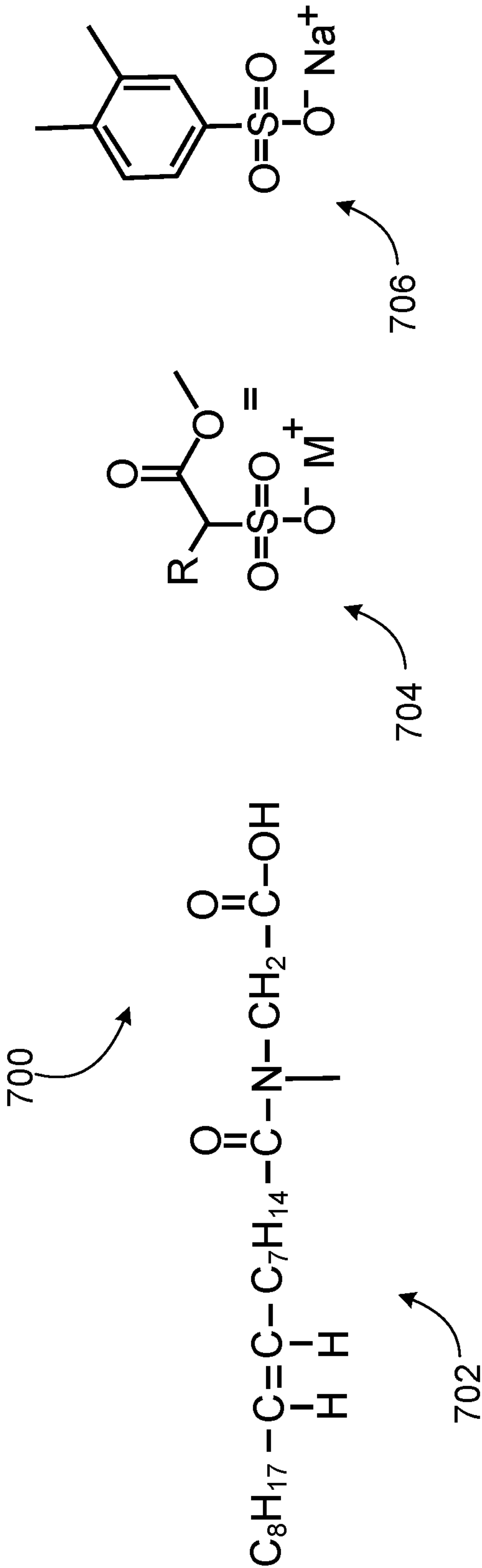


FIG. 7

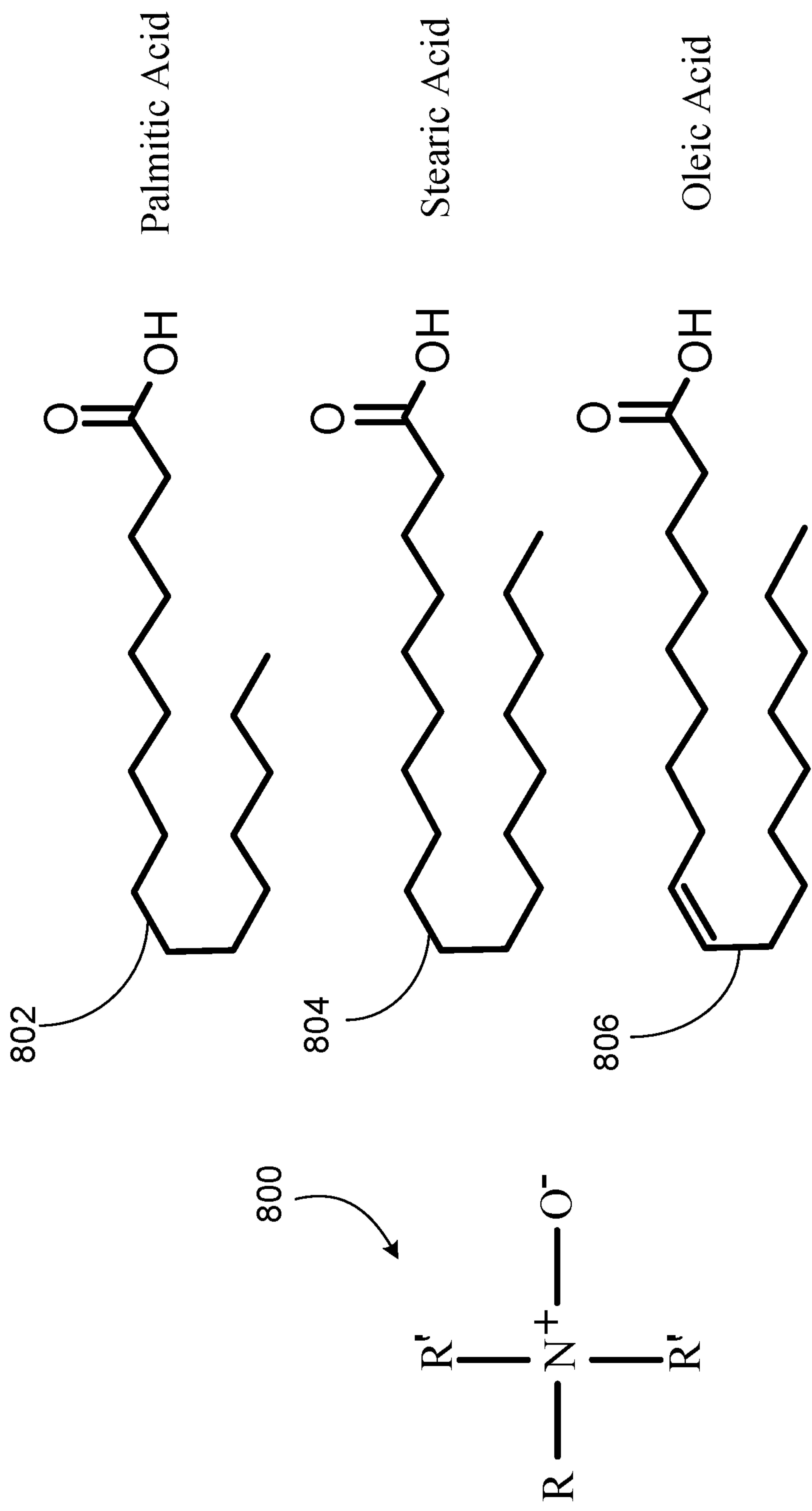


FIG. 8

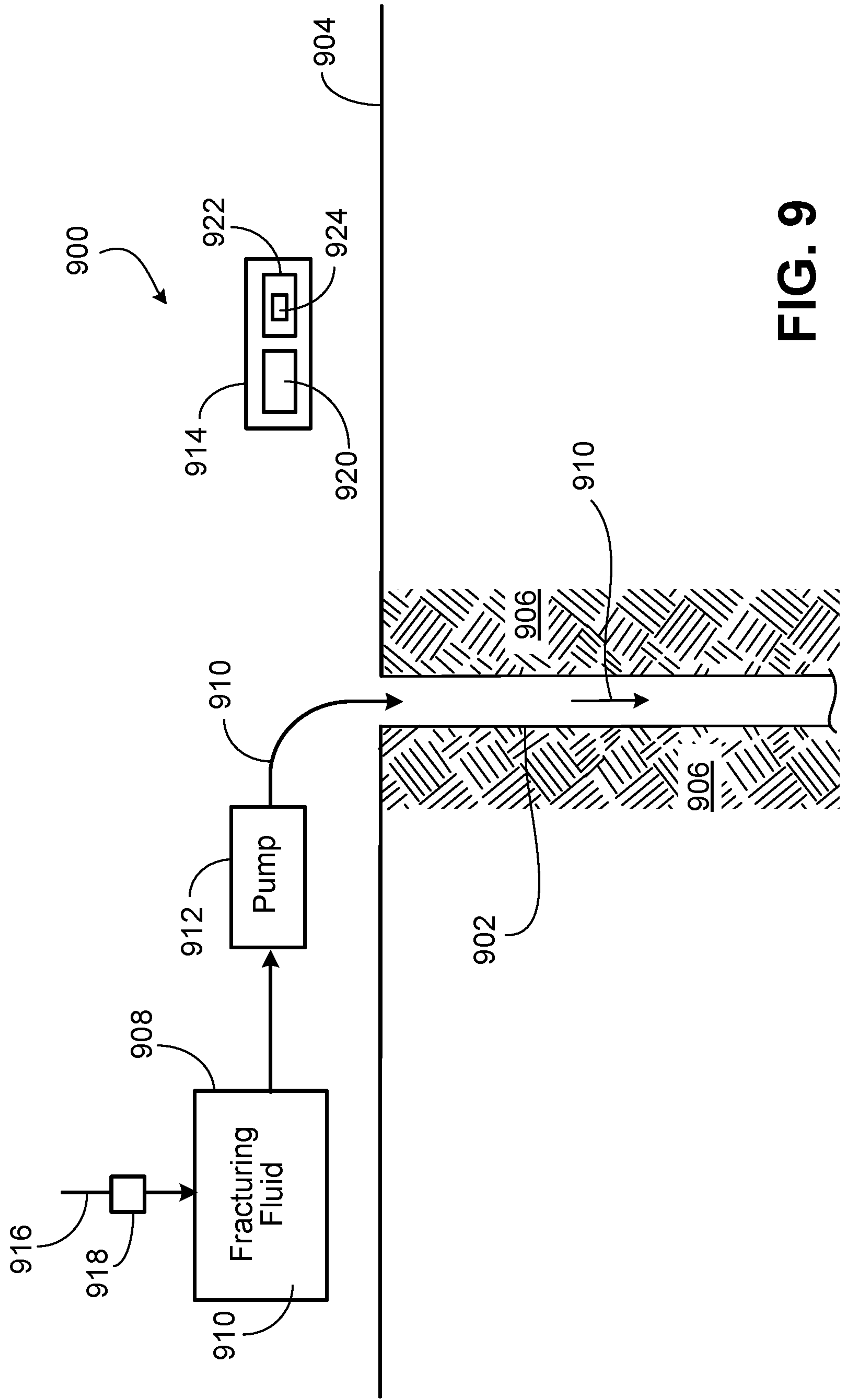
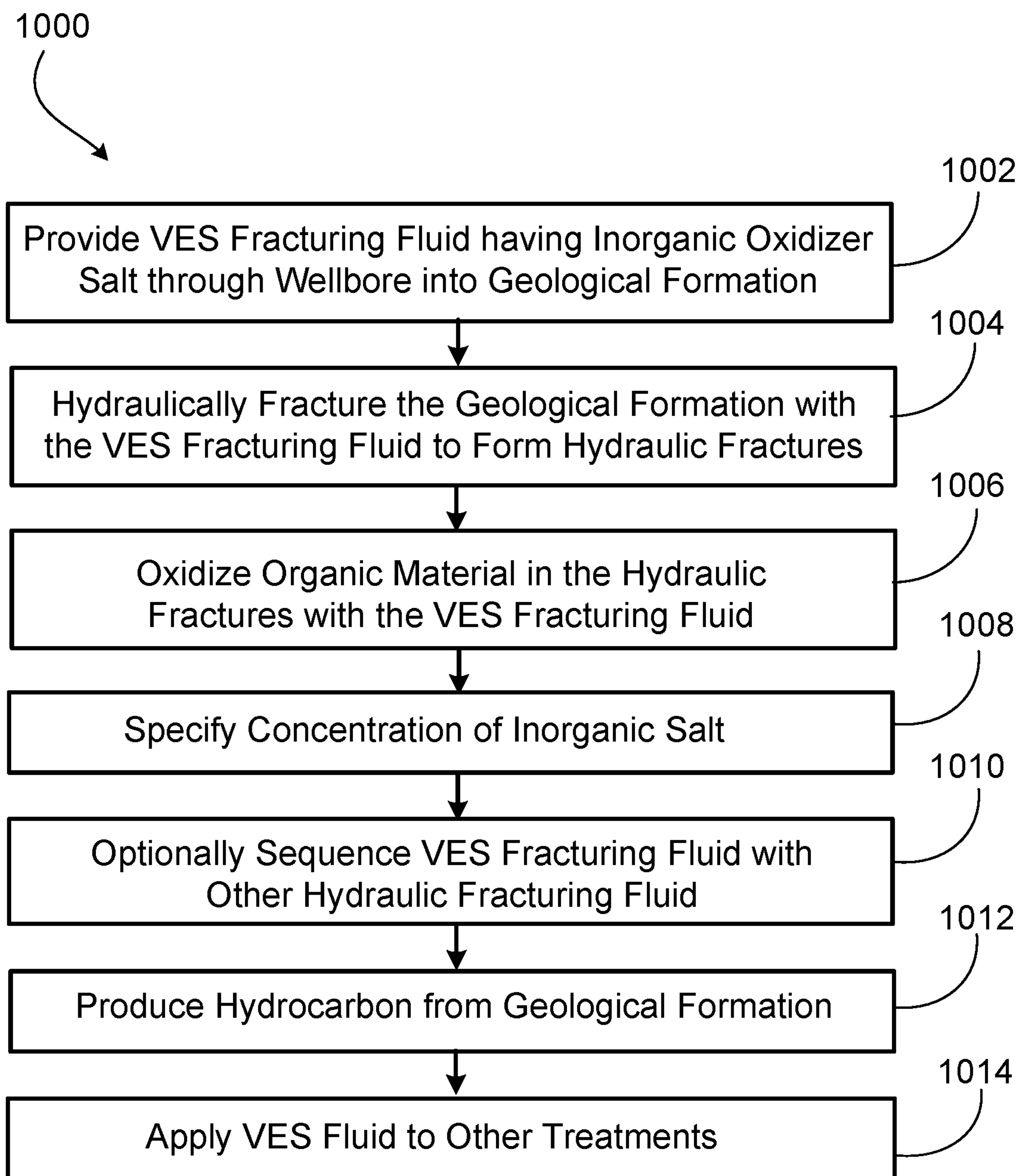


FIG. 9

**FIG. 10**

1102 1104 1100 1106 1110 1112 1114 1116

Table 1. Solution Parameters

Sample	Water (mL)	VES (mL)	CaCl ₂ •2H ₂ O (g)	CaCl ₂ (m)	NaBrO ₃ (g)	NaBrO ₃ (m)	Total ion molality
1	135	7.5	7.5	0.34	0	0	1.02
2	135	7.5	7.5	0.35	3.75	0.166	1.35
3	135	7.5	0	0	15.5	0.685	1.37

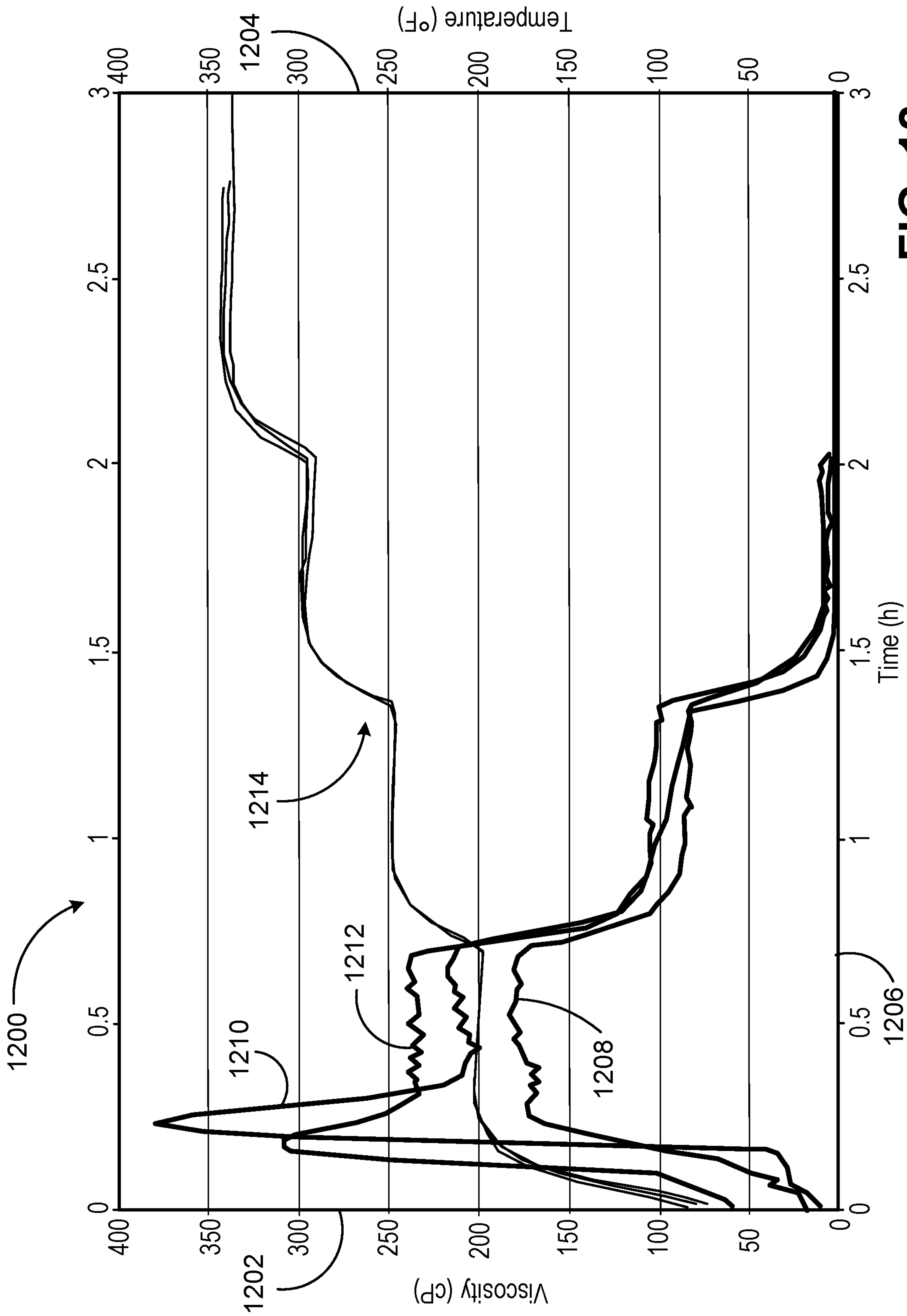
FIG. 11

1302 1304 1306 1308 1310 1312 1300

Table 2. Solution Parameters

Sample	Water (mL)	VES (mL)	Volume of Polymer Added	NaBrO ₃ (g)	NaBrO ₃ (m)
4	135	7.5	1.5 mL	15.5	0.685
5	135	7.5	3.0 mL	15.5	0.685
6	135	7.5	4.5 mL	15.5	0.685

FIG. 13



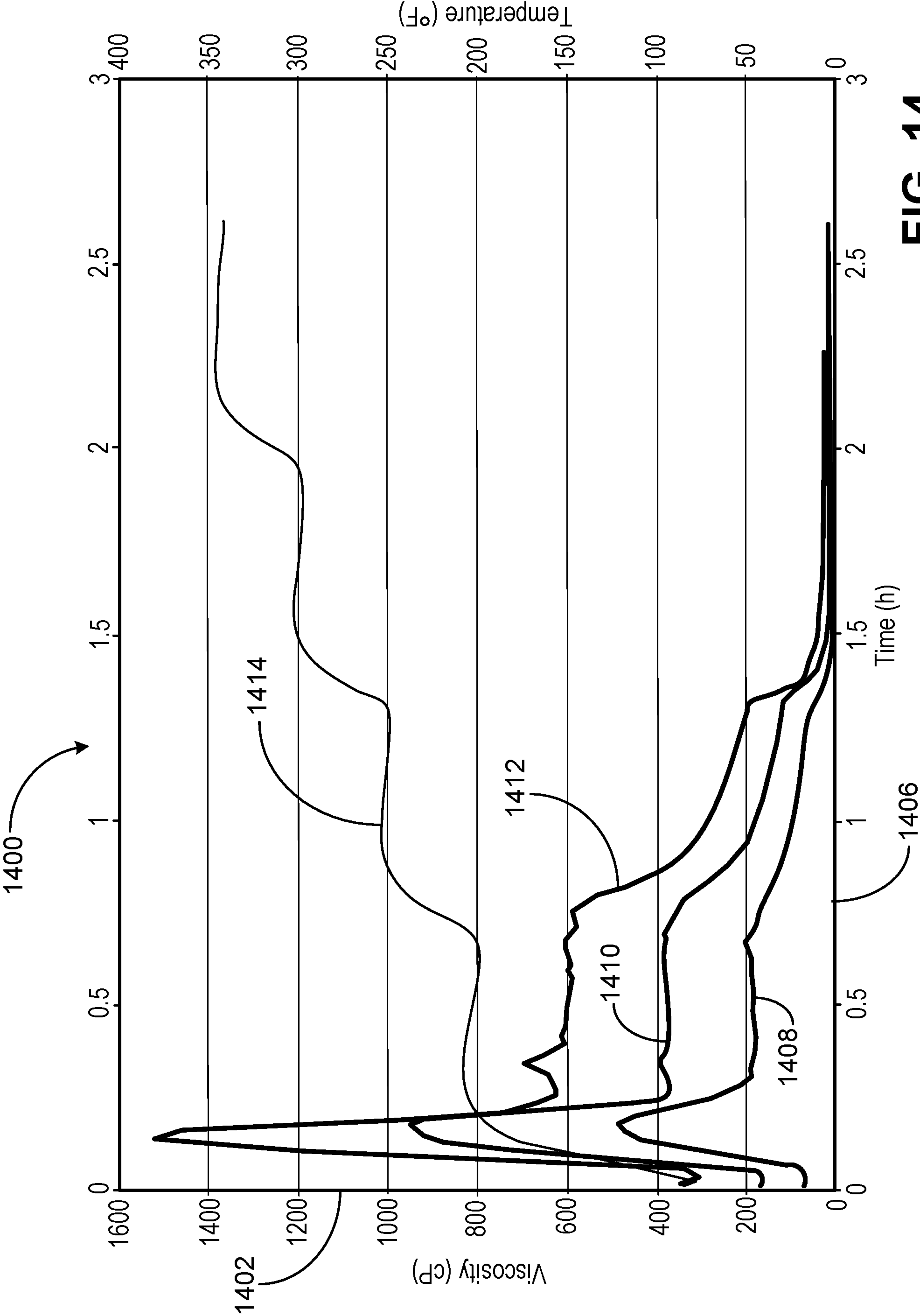


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2020/067357

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C09K8/66	C09K8/68
		E21B43/26
		C09K8/524
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C09K E21B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/035253 A2 (SCHLUMBERGER CA LTD [CA]; SCHLUMBERGER SERVICES PETROL [FR] ET AL.) 27 March 2008 (2008-03-27)	26-51,58
A	* page 6, paragraph [0046], page 7, paragraph [0048] through page 8, paragraph [0049], Examples, claims *	1-25, 52-57

A	WO 2019/140058 A1 (SAUDI ARABIAN OIL CO [SA]; ARAMCO SERVICES CO [US]) 18 July 2019 (2019-07-18) the whole document	1-25

A	WO 2017/040824 A1 (SAUDI ARABIAN OIL CO [SA]; ARAMCO SERVICES CO [US]) 9 March 2017 (2017-03-09) the whole document	1-25

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☒ Further documents are listed in the continuation of Box C.		
☒ See patent family annex.		
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"A" document defining the general state of the art which is not considered to be of particular relevance		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date		"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means		"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search		Date of mailing of the international search report
20 April 2021		29/04/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Nemes, Csaba A.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/067357

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/088476 A2 (CHEVRON USA INC [US]; WIGAND MARCUS [US] ET AL.) 28 June 2012 (2012-06-28) the whole document -----	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/067357

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WO 2019140058 A1	18-07-2019	CA 3090212 A1 US 2019211658 A1 WO 2019140058 A1	18-07-2019 11-07-2019 18-07-2019

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