The present invention relates to viscosified treatment fluids comprising gelling agents that comprise scleroglucan or diutan, and their use in industrial and oil field operations. In certain embodiments, the present invention provides methods of treating a portion of a subterranean formation with a viscosified treatment comprising a gelling agent that comprises scleroglucan or diutan. Methods of fracturing, gravel packing, and producing hydrocarbons also are provided. Viscosified treatment fluid compositions and methods of making such exemplary compositions are provided as well.
VISCOSIFIED TREATMENT FLUIDS
COMPRISING SCLEROGUCAN OR DIUTAN AND ASSOCIATED METHODS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to viscous treatment fluids used in industrial and oil field operations, and more particularly, to viscous treatment fluids comprising gelling agents that comprise scleroglucan or diutan, and their use in industrial and oil field operations.

[0002] In industrial and oil field operation, viscousified treatment fluids are often used to carry particulates into subterranean formations for various purposes, e.g., to deliver particulates to a desired location within a well bore. Examples of subterranean operations that use such viscousified treatment fluids include servicing and completion operations such as fracturing and gravel packing. In fracturing, generally, a viscousified fracturing fluid is used to carry proppant to fractures within the formation, inter alia, to maintain the integrity of those fractures to enhance the flow of desirable fluids to a well bore. In sand control operations such as gravel packing operations, oftentimes a screen, slotted liner, or other mechanical device is placed into a portion of a well bore. A viscousified gravel pack fluid is used to deposit particulates referred to as gravel into the annulus between the mechanical device and the formation or casing to inhibit the flow of particulates from a portion of the subterranean formation to the well bore.

[0003] In most instances, a viscousified treatment fluid should maintain its viscosity in a subterranean operation until that operation is completed, after which the fluid may be “broken” (i.e., its viscosity may be reduced), e.g., so as to drop particulates from the fluid into a desired location within the subterranean formation and/or to reclaim it from the subterranean formation.

[0004] The treatment fluids used in subterranean operations are predominantly water-based liquids comprising polymeric gelling agents that may increase their viscosities, inter alia, to enhance the treatment fluids’ sand suspension capabilities. These gelling agents are usually biopolymers or synthetic polymers that, when hydrated and at a sufficient concentration, are capable of forming a viscous solution. Common gelling agents include polysaccharides such as galactomannan gums, cellulose polymers, and xanthan. Viscousified treatment fluids comprising xanthan generally have sufficient sand suspension properties for lower temperature operations. At elevated temperatures (e.g., those above about 200°F), however, the sand suspension properties of such xanthan treatment fluids are diminished. Consequently, xanthan may not be a suitable gelling agent for viscousified treatment fluids, such as fracturing fluid or gravel pack fluids, when those fluids are used in well bores that comprise elevated temperatures.

SUMMARY OF THE INVENTION

[0005] The present invention relates to viscousified treatment fluids used in industrial and oil field operations, and more particularly, to viscousified treatment fluids comprising gelling agents that comprise scleroglucan or diutan, and their use in industrial and oil field operations.

[0006] In one embodiment, the present invention provides a method of treating a portion of a subterranean formation comprising the steps of: providing a viscousified treatment fluid that comprises a gelling agent that comprises diutan; treating the portion of the subterranean formation; and reducing the viscosity of the viscousified treatment fluid using a breaker that comprises a peroxide.

[0007] In another embodiment, the present invention provides a method of reducing the viscosity of a viscousified treatment fluid that comprises a gelling agent that comprises diutan comprising contacting the viscousified treatment fluid with a breaker that comprises a peroxide.

[0008] In another embodiment, the present invention provides a method of making a viscousified treatment fluid comprising diutan comprising the step of dissolving diutan in an aqueous fluid to form a viscousified treatment fluid comprising diutan.

[0009] In another embodiment, the present invention provides a method of placing a gravel pack in a portion of a subterranean formation comprising: providing a viscousified gravel pack fluid comprising gravel and a gelling agent that comprises diutan; contacting the portion of the subterranean formation with the viscousified gravel pack fluid so as to place a gravel pack in or near a portion of the subterranean formation; and reducing the viscosity of the viscousified gravel pack fluid with a breaker comprising a peroxide.

[0010] In another embodiment, the present invention provides a method of fracturing a portion of a subterranean formation comprising: providing a viscousified fracturing fluid comprising a gelling agent that comprises diutan; contacting the portion of the subterranean formation with the viscousified fracturing fluid at a sufficient pressure to create or enhance at least one fracture in the subterranean formation; and reducing the viscosity of the viscousified fracturing fluid with a breaker comprising a peroxide.

[0011] In another embodiment, the present invention provides a method of treating a portion of a subterranean formation comprising: providing a viscousified treatment fluid comprising a gelling agent that comprises scleroglucan; and treating at least a portion of the subterranean formation with the viscousified treatment fluid.

[0012] In another embodiment, the present invention provides a method of fracturing a portion of a subterranean formation comprising: providing a viscousified fracturing fluid comprising a gelling agent that comprises scleroglucan; and contacting the portion of the subterranean formation with the viscousified fracturing fluid at a sufficient pressure to create or enhance at least one fracture in the subterranean formation.

[0013] In another embodiment, the present invention provides a method of producing hydrocarbons from a subterranean formation wherein a viscousified treatment fluid comprising a gelling agent that comprises scleroglucan is used.

[0014] In another embodiment, the present invention provides a method of producing hydrocarbons from a subterranean formation wherein a viscousified treatment fluid comprising a gelling agent that comprises diutan is used and the subterranean formation has a temperature greater than or equal to 200°F.

[0015] In another embodiment, the present invention provides a method of producing hydrocarbons from a subterranean formation wherein a viscousified treatment fluid com-
prising a gelling agent that comprises diutan and a breaker that comprises a peroxide are used.

[0016] In another embodiment, the present invention provides a subterranean well treatment system comprising a viscosified treatment fluid that comprises diutan and a breaker that comprises a peroxide breaker.

[0017] In another embodiment, the present invention provides a subterranean well treatment fluid comprising a gelling agent that comprises scleroglucan.

[0018] In another embodiment, the present invention provides a method of making a treatment fluid comprising a scleroglucan gelling agent comprising: dissolving scleroglucan in water to produce a solution; neutralizing the solution from a pH of about 13 to one of a pH of less than about 12 to form a viscosified treatment fluid comprising a scleroglucan gelling agent.

[0019] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0020] The present invention relates to viscosified treatment fluids used in industrial and oil field operations, and more particularly, to viscosified treatment fluids comprising gelling agents that comprise scleroglucan or diutan, and their use in industrial and oil field operations. In certain embodiments, the present invention provides compositions and methods that are especially suitable for use in well bores comprising elevated temperatures such as those above 200°F.

[0021] The viscosified treatment fluids of the present invention generally comprise an aqueous base fluid and a gelling agent that comprises scleroglucan or diutan. The viscosified treatment fluids of the present invention may vary widely in density. One of ordinary skill in the art with the benefit of this disclosure will recognize the particular density that is most appropriate for a particular application. The density of the viscosified treatment fluids of the present invention may range from about 8.4 pounds per gallon ("ppg") to about 20.5 ppg. The desired density for a particular viscosified treatment fluid may depend on characteristics of the subterranean formation, including, inter alia, the hydrostatic pressure required to control the fluids of the subterranean formation during placement of the viscosified treatment fluids, and the hydrostatic pressure which will damage the subterranean formation. The gelling agents of the present invention that comprise diutan may be useful in a wide variety of subterranean treatment operations. The gelling agents of the present invention that comprise scleroglucan, although useful in a wide variety of subterranean treatment operations, may be most suited for stimulation operations and the like.

[0022] Scleroglucan is a neutral fungal polysaccharide. Scleroglucan is a hydrophilic colloid, which has a tendency to thicken and stabilize water-based systems by conferring on them a relatively high viscosity, generally higher than that obtained in the case of xanthan, for example, at temperatures at or above about 200°F, for identical concentrations of active compounds. Scleroglucan also appears to be more resistant to pH and temperature changes than xanthan, and therefore, may impart more stable viscosities in such conditions. In certain aspects, the viscosity of a scleroglucan fluid may be virtually independent of pH between a pH of about 1 and about 12.5 up to a temperature limit of about 270°F. Generally, the main backbone polymer chain of scleroglucan comprises (1→3)-β-D-glucopyranosyl units with a single β-D-glucopyranosyl group attached to every third unit on the backbone. Scleroglucan is thought to be resistant to degradation, even at high temperatures such as those at or above about 200°F, even after, e.g., 500 days in seawater. Viscosity data (see Table 1 and Table 2) show that dilute solutions (e.g., about 0.5%) may be shear thinning and stable to at least 250°F. These viscosities illustrate, inter alia, scleroglucan’s suitability for sand suspension and transport applications.

TABLE 1

<table>
<thead>
<tr>
<th>Shear Rate (s⁻¹)</th>
<th>70°C</th>
<th>80°C</th>
<th>90°C</th>
<th>108°C</th>
<th>118°C</th>
<th>127°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>1500</td>
<td>1480</td>
<td>1460</td>
<td>1330</td>
<td>1540</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>520</td>
<td>540</td>
<td>540</td>
<td>550</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>180</td>
<td>180</td>
<td>178</td>
<td>175</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>98</td>
<td>99</td>
<td>93</td>
<td>92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2

<table>
<thead>
<tr>
<th>Elastic Moduli G’ (Pa) Measured Using a Haake RS 150 Controlled Stress Rheometer at 25°C; Measurements Made at 1 Hz in the Linear Viscoelastic Region.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthan</td>
</tr>
<tr>
<td>1.0%</td>
</tr>
<tr>
<td>0.5%</td>
</tr>
</tbody>
</table>

[0024] Diutan gum is a polysaccharide designated S-657, which is prepared by fermentation of a strain of sphingomonas. Its structure has been elucidated as a hexaasaccharide having a tetrasaccharide repeat unit in the backbone that comprises glucose and rhamnose units and di-rhamnose side chain. It is believed to have thickening, suspending, and stabilizing properties in aqueous solutions. Polysaccharide S-657 is composed principally of carbohydrates, about 12% protein, and about 7% (calculated as O-acetyl) acyl groups, the carbohydrate portion containing about 19% glucuronic acid, and the neutral sugars rhamnose and glucose in the approximate molar ratio of about 2:1. Details of the diutan gum structure may be found in an article by Diltz et al., “Location of O-acetyl Groups in S-657 Using the Reductive-Cleave Method,” CARBOHYDRATE RESEARCH, Vol. 331, p. 265-270 (2001), which is hereby incorporated by reference in its entirety. Details of preparing diutan gum may be found in U.S. Pat. No. 5,175,278, which is hereby incorporated by reference in its entirety. A suitable source of diutan is “GOVIS XI,” which is commercially available from Kelco Oil Field Group, Houston, Tex. The elastic moduli of some diutan solutions as compared to xanthan solutions are shown in Table 3.
TABLE 3

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>G'(Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Diutan in water</td>
<td>15.0</td>
</tr>
<tr>
<td>0.5% Xanthan in water</td>
<td>11.8</td>
</tr>
<tr>
<td>0.5% Diutan in 6% NaCl</td>
<td>19.0</td>
</tr>
<tr>
<td>0.5% Xanthan in 6% NaCl</td>
<td>12.8</td>
</tr>
<tr>
<td>0.75% Diutan in water</td>
<td>33.0</td>
</tr>
<tr>
<td>0.75% of Diutan in 20% KCl</td>
<td>29.0</td>
</tr>
</tbody>
</table>

The aqueous base fluids of the treatment fluids of the present invention generally comprise fresh water, salt water, or a brine (e.g., a saturated salt water). Other water sources may be used, including those comprising divalent or trivalent cations, e.g., magnesium, calcium, zinc, or iron. If a water source is used which contains such divalent or trivalent cations in concentrations sufficiently high to be problematic, then such divalent or trivalent salts may be removed, either by a process such as reverse osmosis, or by raising the pH of the water in order to precipitate out such divalent salts to lower the concentration of such salts in the water before the water is used. Monovalent brines are preferred and, where used, may be of any weight. Salts may be added to the water source, inter alia, to provide a brine to produce a treatment fluid having a desired density or other characteristics. One of ordinary skill in the art with the benefit of this disclosure will recognize the particular type of salt appropriate for a particular application, given considerations such as protection of the formation, the presence or absence of reactive clays in the formation adjacent to the well bore, and the factors affecting wellhead control. A wide variety of salts may be suitable. Examples of suitable salts include, inter alia, potassium chloride, sodium bromide, ammonium chloride, cesium formate, potassium formate, sodium formate, sodium nitrate, calcium bromide, zinc bromide, and sodium chloride. An artisan of ordinary skill with the benefit of this disclosure will recognize the appropriate concentration of a particular salt to achieve a desired density given factors such as the environmental regulations that may prevail. Also, the composition of the water used also will dictate whether and what type of salt is appropriate.

In certain embodiments, the viscosified treatment fluids of the present invention also may comprise pH control additives, surfactants, breakers, bactericides, crosslinkers, fluid loss control additives, stabilizers, combinations thereof, or the like. In a preferred embodiment, a gelling agent comprising diutan and a breaker comprising a peroxide are included in a treatment fluid of the present invention.

Suitable pH control additives, in certain embodiments, may comprise bases, chelating agents, acids, or combinations of chelating agents and acids or bases. A pH control additive may be necessary to maintain the pH of the treatment fluid at a desired level, e.g., to improve the dispersion of the gelling agent in the aqueous base fluid. In some instances, it may be beneficial to maintain the pH at neutral or above 7.

In some embodiments, the pH control additive may be a chelating agent. When added to the treatment fluids of the present invention, such a chelating agent may chelate any dissolved iron that may be present in the water. Such chelating may prevent free iron from crosslinking the gelling agent molecules. Such crosslinking may be problematic because, inter alia, it may cause severe filtration problems. Any suitable chelating agent may be used with the present invention. Examples of suitable chelating agents include an anhydrous form of citric acid, commercially available under the tradename “FE-2™” Iron Sequestering Agent from Halliburton Energy Services, Inc., of Duncan, Okla. Another example of a suitable chelating agent is a solution of citric acid dissolved in water, commercially available under the tradename “FE-2A™” from Halliburton Energy Services, Inc., of Duncan, Okla. Other chelating agents that are suitable for use with the present invention include, inter alia, nitritotriacetic acid and any acid form of ethylene diamine tetracetic acid (“EDTA”). Generally, the chelating agent is present in an amount sufficient to prevent crosslinking of the gelling agent molecules by any free iron that may be present.

In one embodiment, the chelating agent may be present in an amount of from about 0.02% to about 2.0% by weight of the treatment fluid. In another embodiment, the chelating agent is present in an amount in the range of from about 0.02% to about 0.5% by weight of the treatment fluid. One of ordinary skill in the art with the benefit of this disclosure will be able to determine the proper concentration of chelating agents for a particular application.

In another embodiment, the pH control additive may be an acid. Any known acid may be suitable with the treatment fluids of the present invention. Examples of suitable acids include, inter alia, hydrochloric acid, acetic acid, formic acid and citric acid.

The pH control additive also may comprise a base to elevate the pH of the mixture that is formed once the gelling agent has been added to and dispersed within the treatment fluid. It may be desirable to elevate the pH of the mixture, inter alia, to achieve a desired dispersion of the gelling agent. Generally, a base may be used to elevate the pH of the mixture to greater than or equal to about 7. In one embodiment, a base may be used to elevate the pH of the mixture to greater than or equal to about 13. Any known base that is compatible with the gelling agents of the present invention can be used in the viscosified treatment fluids of the present invention. Examples of suitable bases include sodium hydroxide, potassium carbonate, potassium hydroxide and sodium carbonate. An example of a suitable base is a solution of 25% sodium hydroxide commercially available from Halliburton Energy Services, Inc., of Duncan, Okla., under the tradename “MO-67™” pH Controlling Additive. One of ordinary skill in the art with the benefit of this disclosure will recognize the suitable bases that may be used to achieve a desired pH elevation.

In still another embodiment, the pH control additive may comprise a combination of an acid and a chelating agent or a base and a chelating agent. Such combinations may be suitable when, inter alia, the addition of a chelating agent (in an amount sufficient to chelate the iron present) is insufficient by itself to achieve the desired pH reduction.

In some embodiments, the viscosified treatment fluids of the present invention may include surfactants, e.g., to improve the compatibility of the viscosified treatment fluids of the present invention with other fluids (like any formation fluids) that may be present in the well bore. An artisan of ordinary skill with the benefit of this disclosure
will be able to identify the type of surfactant as well as the appropriate concentration of surfactant to be used. Suitable surfactants may be used in a liquid or powder form. Where used, the surfactants are present in the viscosified treatment fluid in an amount sufficient to prevent incompatibility with formation fluids or well bore fluids. In an embodiment where liquid surfactants are used, the surfactants are generally present in an amount in the range of from about 0.01% to about 5.0% by volume of the viscosified treatment fluid. In one embodiment, the liquid surfactants are present in an amount in the range of from about 0.1% to about 2.0% by volume of the viscosified treatment fluid. In embodiments where powdered surfactants are used, the surfactants may be present in an amount in the range of from about 0.001% to about 0.5% by weight of the viscosified treatment fluid.

Examples of suitable surfactants are non-emulsifiers commercially available from Halliburton Energy Services, Inc., of Duncan, Okla., under the tradenames “LOSURF-250™,” “LOSURF-300™,” “LOSURF-357™,” and “LOSURF-400™.” Another example of a suitable surfactant is a non-emulsifier commercially available from Halliburton Energy Services, Inc., of Duncan, Okla., under the tradename “NEA-96MT™” Surfactant.

[0033] In some embodiments, the viscosified treatment fluids of the present invention may contain bactericides, inter alia, to protect both the subterranean formation as well as the viscosified treatment fluid from attack by bacteria. Such attacks may be problematic because they may lower the viscosity of the viscosified treatment fluid, resulting in poorer performance, such as poorer sand suspension properties, for example. Any bactericides known in the art are suitable. An artisan of ordinary skill with the benefit of this disclosure will be able to identify a suitable bactericide and the proper concentration of such bactericide for a given application. Where used, such bactericides are present in an amount sufficient to destroy all bacteria that may be present. Examples of suitable bactericides include 2,2-dibromo-3-nitropropionamide, commercially available under the tradename “BE-35™” Surfactant from Halliburton Energy Services, Inc., of Duncan, Okla., and a 2-bromo-2-nitro-1,3-propanediol commercially available under the tradename “BE-6™” Surfactant from Halliburton Energy Services, Inc., of Duncan, Okla. In one embodiment, the bactericides are present in the viscosified treatment fluid in an amount in the range of from about 0.001% to about 0.003% by weight of the viscosified treatment fluid. Another example of a suitable bactericide is a solution of sodium hypochlorite, commercially available under the tradename “CAI-1™” chemical from Halliburton Energy Services, Inc., of Duncan, Okla. In certain embodiments, such bactericides may be present in the viscosified treatment fluid in an amount in the range of from about 0.01% to about 0.1% by volume of the viscosified treatment fluid. In certain preferred embodiments, when bactericides are used in the viscosified treatment fluids of the present invention, they are added to the viscosified treatment fluid before the gelling agent is added.

[0034] The viscosified treatment fluids of the present invention also (optionally) may comprise a crosslinker to crosslink the polymeric components of the gelling agent in the viscosified treatment fluid. Suitable crosslinkers include boron derivatives; potassium derivatives, including but not limited to, potassium periodate or potassium iodate; ferric iron derivatives; magnesium derivatives; and the like. Such crosslinking of the polymeric components of the gelling agent may be desirable where it is desirable to make a treatment fluid more viscous. One of ordinary skill in the art with the benefit of this disclosure will recognize when such crosslinkers are appropriate and what particular crosslinker will be most suitable. It should be noted that suitable viscosities could be obtained for viscosified treatment fluids that comprise gelling agents that comprise diutan without using crosslinkers.

[0035] The viscosified treatment fluids of the present invention also may comprise breakers capable of reducing the viscosity of the viscosified treatment fluid at a desired time. Examples of such suitable breakers for viscosified treatment fluids of the present invention that include a gelling agent that comprises scleroglucan include, but are not limited to, sodium chloride, hypochlorite, perborate, persulfates, peroxides, including organic peroxides. Other suitable breakers include suitable acids. Preferred examples of suitable breakers for viscosified treatment fluids of the present invention that include a gelling agent that comprises diutan include peroxide breakers. Preferred examples include tert-butyl hydroperoxide and tert-amyl hydroperoxide. Sodium persulfate and sodium chloride are not preferred breakers for viscosified treatment fluids of the present invention that include a gelling agent that comprises diutan because optimal degradation generally may not occur within a desirable time period. A breaker may be included in a viscosified treatment fluid of the present invention in an amount and form sufficient to achieve the desired viscosity reduction at a desired time. The breaker may be formulated to provide a delayed break, if desired. For example, a suitable breaker may be encapsulated if desired. Suitable encapsulation methods are known to those skilled in the art. One suitable encapsulation method that may be used involves coating the chosen breakers with a material that will degrade when downhole so as to release the breaker when desired. Resins that may be suitable include, but are not limited to, polymeric materials that will degrade when downhole. The terms “degrade,” “degradation,” or “degradable” refer to both the two relatively extreme cases of hydrolytic degradation that the degradable material may undergo, i.e., heterogeneous (or bulk erosion) and homogeneous (or surface erosion), and any stage of degradation in between these two. This degradation can be a result of, inter alia, a chemical or thermal reaction or a reaction induced by radiation. Suitable examples include polysaccharides such as dextran or cellulose; chitin; chitosan; proteins; aliphatic polyesters; poly(lactides); poly(glycolides); poly(ε-caprolactones); poly(hydroxybutyrate); poly(anhydrides); aliphatic polycarbonates; orthoesters, poly(orthoesters); poly(amino acids); poly(ethylene oxides); and polyphosphazenes. If used, a breaker should be included in a composition of the present invention in an amount sufficient to facilitate the desired reduction in viscosity in a viscosifier treatment fluid. For instance, peroxide concentrations that may be used vary from about 0.1 to about 10 gallons of peroxide per 1000 gallons of the viscosified treatment fluid. Optionally, the viscosified treatment fluid may contain an activator or a retarder, inter alia, to optimize the break rate provided by the breaker. Any known activator or retarder that is compatible with the particular breaker used is suitable for use in the present invention. Examples of such suitable activators include, but are not limited to, chelated iron, copper, cobalt, and reducing sugars. An example of a suitable retarder includes sodium thiosulfate diethylene tri-
amine. In some embodiments, the sodium thiosulfate may be used in a range of from about 5 to about 2000 lbs. per 1000 gallons of viscosified treatment fluid. An artisan of ordinary skill with the benefit of this disclosure will be able to identify a suitable activator or retarder and the proper concentration of such activator or retarder for a given application.

[0036] If desired, stabilizers may be added to the viscosified treatment fluids of the present invention, e.g., in high-temperature gravel packing operations. Suitable stabilizers include sodium thiosulfate. Such stabilizers may be useful when the viscosified treatment fluids of the present invention are utilized in a subterranean formation having a temperature above about 200°F.

[0037] In certain preferred embodiments, certain embodiments of the viscosified treatment fluids of the present invention may be prepared according to the following process. The scleroglucan may be dissolved in water or a salt solution (e.g., a 20% KCl salt solution) or preferably in a solution at a pH of about 13. The solution is then neutralized to a pH below about 12, and then salt may be added. This process is suitable for viscosified treatment fluids comprising a concentration of scleroglucan from about 0.1% to about 10% of the viscosified treatment fluid.

[0038] In certain preferred embodiments, diutan may be dissolved in water or salt solutions. For instance, diutan dissolves in water or 20% KCl by simply stirring.

[0039] In one embodiment, the present invention provides a method of treating a portion of a subterranean formation comprising the steps of: providing a viscosified treatment fluid that comprises a gelling agent that comprises diutan; treating the portion of the subterranean formation; and reducing the viscosity of the viscosified treatment fluid using a breaker that comprises a peroxide.

[0040] In another embodiment, the present invention provides a method of making a viscosified treatment fluid comprising diutan comprising the step of dissolving diutan in an aqueous fluid to form a viscosified treatment fluid comprising diutan.

[0041] In another embodiment, the present invention provides a method of placing a gravel pack in a portion of a subterranean formation comprising: providing a viscosified gravel pack fluid comprising gravel and a gelling agent that comprises diutan; contacting the portion of the subterranean formation with the viscosified gravel pack fluid so as to place a gravel pack in or near a portion of the subterranean formation; and reducing the viscosity of the viscosified gravel pack fluid with a breaker comprising a peroxide.

[0042] In another embodiment, the present invention provides a method of fracturing a portion of a subterranean formation comprising: providing a viscosified fracturing fluid comprising a gelling agent that comprises diutan; contacting the portion of the subterranean formation with the viscosified fracturing fluid at a sufficient pressure to create or enhance at least one fracture in the subterranean formation; and reducing the viscosity of the viscosified fracturing fluid with a breaker comprising a peroxide.

[0043] In another embodiment, the present invention provides a method of treating a subterranean formation comprising: providing a viscosified treatment fluid comprising a gelling agent that comprises scleroglucan; and treating at least a portion of the subterranean formation with the viscosified treatment fluid.

[0044] In another embodiment, the present invention provides a method of fracturing a portion of a subterranean formation comprising: providing a viscosified fracturing fluid comprising a gelling agent that comprises scleroglucan; and contacting the portion of the subterranean formation with the viscosified fracturing fluid at a sufficient pressure to create or enhance at least one fracture in the subterranean formation.

[0045] In another embodiment, the present invention provides a subterranean well stimulation or completion fluid comprising a viscosified treatment fluid that comprises diutan and a breaker that comprises a peroxide breaker.

[0046] In another embodiment, the present invention provides a method of making a treatment fluid comprising a scleroglucan gelling agent comprising: dissolving scleroglucan in water to produce a solution; neutralizing the solution from a pH of about 13 to one of a pH of less than about 12 to form a viscosified treatment fluid comprising a scleroglucan gelling agent.

[0047] To facilitate a better understanding of the present invention, the following examples of some of the preferred embodiments are given. In no way should such examples be read to limit, or define, the scope of the invention.

EXAMPLES

[0050] Solutions of diutan in water at room temperature show an elastic rheological modulus (G') of 15 Pa at 0.5%, while at 0.75% G' is 33 Pa. Sand suspension tests at 220°F shows that the diutan viscosified treatment fluid suspends sand for at least 2 hours. Thus, a viscosified treatment fluid of the present invention comprising diutan is satisfactory for suspending particulates such as proppant or gravel that may be used in subterranean operations.

[0051] To illustrate, inter alia, the breaking characteristics of diutan with various oxidizing and breaking agents (referred to as “breakers” below), the following tests were performed. “GEOVIS XT” (commercially available from Kelco Oil Field Group, Houston, Tex.) was the source of the diutan polymers used in these examples.

[0052] Sodium persulfate at about 1 pound to about 1000 gallons is well known to effectively degrade guar and guar derivatives at temperatures above about 135°F. Various concentrations of sodium persulfate breaker were tried initially with a solution of GEOVIS XT (0.7 g) dissolved in KCl/NaCl brine (200 ml of 9.7 lbs./gal). The GEOVIS XT was dissolved in the brine, the sodium persulfate breaker was added, and the resulting solution was kept at 230°F for a
24 hours. The solutions were cooled before the viscosities were measured at ambient temperatures. For comparison, a guar solution of a similar concentration to this sample could have a viscosity of less than 2 cP after 24 hours of treatment at 230° F with lb./1000 gal of a sodium persulfate breaker. The results are shown in Table 4 below.

![Table 4](image)

As can be seen by the data in Table 4, the GEOVIS XT appears to be relatively poorly degraded by the sodium persulfate breaker.

In other sets of experiments, tert-butyl hydroperoxide was used as the breaker. As described above, the GEOVIS XT was dissolved in the brine, the tert-butyl hydroperoxide breaker was added, and the resulting solution was kept at 230° F for 24 hours. The solutions were cooled and then their viscosities were measured at ambient temperature. Viscosities were measured using a Chan 35 viscometer at 300 rpm at ambient temperature. The results are shown in Table 5 below.

![Table 5](image)

As can be seen from Table 5, the degradation of the GEOVIS XT using a tert-butyl hydroperoxide breaker was more effective than using a sodium persulfate breaker.

We have also found that the degradation of GEOVIS XT by a tert-butyl hydroperoxide breaker may be delayed if desired by the inclusion of sodium thiosulfate. This was shown by adding sodium thiosulfate to solutions of GEOVIS XT and a tert-butyl hydroperoxide breaker at 1 gal/1000 gals GEOVIS XT (at 0.36% in KCl brine, having density of 9.7 lbs./gal), and measuring the viscosity as above after storage at 230° F. for various times. The data results are shown in Table 6 below.

![Table 6](image)

As can be seen from the data in Table 6, the addition of sodium thiosulfate appears to retard the degradation of the GEOVIS XT, which may allow the timing of the breaking of the GEOVIS XT to be tuned to suit particular well treatment requirements.

In another set of experiments, tert-amyl hydroperoxide was used as the breaker. In these experiments, GEOVIS XT was dissolved in a KCl solution (1000 ml of 9.7 lbs./gal), and the viscosities were measured on a Chan 35 viscometer at 300 rpm after storage for various times at 230° F. as shown in Table 7. The solutions were cooled before the viscosities were measured at ambient temperatures.

![Table 7](image)

As can be seen from Table 7, tert-amyl hydroperoxide may be an effective breaker for GEOVIS XT.
TABLE 8

<table>
<thead>
<tr>
<th>Sodium Chlorite as Breaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
</tr>
<tr>
<td>Sodium Chlorite Conc. in g/100 ml</td>
</tr>
<tr>
<td>Sodium Chlorite Conc. in g/100 ml</td>
</tr>
<tr>
<td>0.006</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Storage Time</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>21</td>
<td>20</td>
<td>19</td>
<td>19</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>24</td>
<td>20</td>
<td>20</td>
<td>19.5</td>
<td>19.5</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

As shown in Table 8, the results were surprising in that sodium chlorite appeared to have little effect on the degradation of GEOVIS XT, contrary to what would have been expected with a guar viscosifier.

GEOVIS XT has relatively unusual breaking characteristics. GEOVIS XT appears to be unaffected by the commonly used sodium persulfate and sodium chlorite breakers, thought it is degraded by tert-butyl hydroperoxide and tert-amyl hydroperoxide.

Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

What is claimed is:

1. A method of treating a portion of a subterranean formation comprising the steps of:
   - providing a viscosified treatment fluid that comprises a gelling agent that comprises diutan;
   - treating the portion of the subterranean formation; and
   - reducing the viscosity of the viscosified treatment fluid using a breaker that comprises a peroxide.

2. The method of claim 1 wherein the breaker is present in an amount sufficient to reduce the viscosity of the viscosified treatment fluid so as to facilitate the recovery of the fluid at the surface.

3. The method of claim 1 wherein the peroxide is present in an amount of from about 0.1 to about 10 gallons of peroxide per 1000 gallons of the viscosified treatment fluid.

4. The method of claim 1 wherein the viscosified treatment fluid comprises fresh water, salt water, or a brine.

5. The method of claim 1 wherein the viscosified treatment fluid comprises a monovalent brine.

6. The method of claim 1 wherein the viscosified treatment fluid comprises a salt.

7. The method of claim 6 wherein the salt comprises potassium chloride, sodium bromide, ammonium chloride, cesium formate, potassium formate, sodium formate, sodium nitrate, calcium bromide, zinc bromide, or sodium chloride.

8. The method of claim 1 wherein the viscosified treatment fluid comprises a pH control additive, a surfactant, a bactericide, a crosslinker, a fluid loss control additive, or a combination thereof.

9. The method of claim 8 wherein the pH control additive comprises a chelating agent, a base, an acid, a combination of a chelating agent and an acid, or a combination of a chelating agent and a base.

10. The method of claim 1 wherein the breaker comprises tert-butyl hydroperoxide or tert-amyl hydroperoxide.

11. The method of claim 1 wherein the breaker comprises encapsulated breaker particles that comprise a breaker and a coating material.

12. The method of claim 11 wherein the coating material comprises a degradable polymeric material.

13. The method of claim 12 wherein the degradable polymeric material is a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(e-caprolactone), a poly(hydroxybutyrate), a poly(anhydride), an aliphatic polycarbonate, an orthoester, a poly(orthoester), a poly(ether), a poly(ester), a poly(ether), a poly(ester), or a combination thereof.

14. The method of claim 1 wherein the viscosified treatment fluid comprises an activator or a retarder that is compatible with the breaker.

15. The method of claim 14 wherein the retarder comprises sodium thiosulfate.

16. The method of claim 1 wherein the viscosified treatment fluid comprises a stabilizer.

17. The method of claim 16 wherein the stabilizer comprises sodium thiosulfate.

18. A method of reducing the viscosity of a viscosified treatment fluid that comprises a gelling agent that comprises diutan comprising contacting the viscosified treatment fluid with a breaker that comprises a peroxide.

19. The method of claim 18 wherein the breaker is present in an amount sufficient to reduce the viscosity of the viscosified treatment fluid so as to facilitate the recovery of the fluid at the surface.

20. The method of claim 18 wherein the peroxide is present in an amount of from about 0.1 to about 10 gallons of peroxide per 1000 gallons of the viscosified treatment fluid.

21. The method of claim 18 wherein the breaker comprises tert-butyl hydroperoxide or tert-amyl hydroperoxide.
22. The method of claim 18 wherein the breaker comprises encapsulated breaker particles that comprise a breaker and a coating material.

23. The method of claim 22 wherein the coating material comprises a degradable polymeric material.

24. The method of claim 23 wherein the degradable polymeric material is a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(e-caprolactone), a poly(hydroxybutyrate), a poly(anhydride), an aliphatic polycarbonate, an orthoester, a poly(orthoester), a poly(amic acid), a poly(ethylene oxide), a polyphosphazene, or a combination thereof.

25. A method of making a viscousified treatment fluid comprising diutan comprising the step of dissolving diutan in an aqueous fluid to form a viscousified treatment fluid comprising diutan.

26. The method of claim 25 wherein the aqueous fluid comprises a salt.

27. The method of claim 25 wherein the aqueous fluid comprises potassium chloride.

28. The method of claim 25 wherein the aqueous fluid is a 20% potassium chloride solution.

29. The method of claim 25 wherein the viscousified treatment fluid comprising diutan has a density in the range of from about 8.4 pounds per gallon to about 20.5 pounds per gallon.

30. A method of placing a gravel pack in a portion of a subterranean formation comprising:

providing a viscousified gravel pack fluid comprising gravel and a gelling agent that comprises diutan;

contacting the portion of the subterranean formation with the viscousified gravel pack fluid so as to place a gravel pack in or near a portion of the subterranean formation; and

reducing the viscosity of the viscousified gravel pack fluid with a breaker comprising a peroxide.

31. The method of claim 30 wherein the breaker is present in an amount sufficient to reduce the viscosity of the viscousified treatment fluid so as to facilitate the recovery of the fluid at the surface.

32. The method of claim 30 wherein the peroxide is present in an amount of from about 0.1 to about 10 gallons of peroxide per 1000 gallons of the viscousified treatment fluid.

33. The method of claim 30 wherein the breaker comprises tert-butyl hydroperoxide or tert-amyl hydroperoxide.

34. The method of claim 30 wherein the breaker comprises encapsulated breaker particles that comprise a breaker and a coating material.

35. The method of claim 34 wherein the coating material comprises a degradable polymeric material.

36. The method of claim 35 wherein the degradable polymeric material is a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(e-caprolactone), a poly(hydroxybutyrate), a poly(anhydride), an aliphatic polycarbonate, an orthoester, a poly(orthoester), a poly(amic acid), a poly(ethylene oxide), a polyphosphazene, or a combination thereof.

37. The method of claim 30 wherein the viscousified gravel pack fluid has a density of about 8.4 pounds per gallon to about 20.5 pounds per gallon.

38. The method of claim 30 wherein the subterranean formation has a temperature of about 200°F or higher.

39. The method of claim 30 wherein the breaker is present in an amount sufficient to reduce the viscosity of the viscousified gravel pack fluid to facilitate the recovery of the fluid.

40. A method of fracturing a portion of a subterranean formation comprising:

providing a viscousified fracturing fluid comprising a gelling agent that comprises diutan;

contacting the portion of the subterranean formation with the viscousified fracturing fluid at a sufficient pressure to create or enhance at least one fracture in the subterranean formation; and

reducing the viscosity of the viscousified fracturing fluid with a breaker comprising a peroxide.

41. The method of claim 40 wherein the viscousified fracturing fluid comprises proppant.

42. The method of claim 40 wherein the breaker is present in an amount sufficient to reduce the viscosity of the viscousified treatment fluid so as to facilitate the recovery of the fluid at the surface.

43. The method of claim 40 wherein the peroxide is present in an amount of from about 0.1 to about 10 gallons of peroxide per 1000 gallons of the viscousified treatment fluid.

44. The method of claim 40 wherein the breaker comprises tert-butyl hydroperoxide or tert-amyl hydroperoxide.

45. The method of claim 40 wherein the breaker comprises encapsulated breaker particles that comprise a breaker and a coating material.

46. The method of claim 45 wherein the coating material comprises a degradable polymeric material.

47. The method of claim 46 wherein the degradable polymeric material is a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(e-caprolactone), a poly(hydroxybutyrate), a poly(anhydride), an aliphatic polycarbonate, an orthoester, a poly(orthoester), a poly(amic acid), a poly(ethylene oxide), a polyphosphazene, or a combination thereof.

48. The method of claim 40 wherein the viscousified gravel pack fluid has a density of about 8.4 pounds per gallon to about 20.5 pounds per gallon.

49. The method of claim 40 wherein the subterranean formation has a temperature of about 200°F or higher.

50. The method of claim 40 wherein the subterranean formation further comprises a fluid loss control additive.

51. The method of claim 40 wherein the viscousified fracturing fluid further comprises a pH control additive, a surfactant, a bactericide, a crosslinker, a fluid loss control additive, a stabilizer, or a combination thereof.

52. A method of servicing or completing a portion of a subterranean formation comprising:

providing a viscousified treatment fluid comprising a gelling agent that comprises scleroglucan; and

servicing or completing at least a portion of the subterranean formation with the viscousified treatment fluid.

53. The method of claim 52 wherein servicing or completing at least a portion of the subterranean formation involves stimulating at least a portion of the subterranean formation.
54. The method of claim 52 further comprising reducing the viscosity of the viscosified treatment fluid with a breaker after treating the portion of the subterranean formation.

55. The method of claim 54 wherein the breaker comprises encapsulated breaker particles that comprise a breaker and a coating material.

56. The method of claim 55 wherein the coating material comprises a degradable polymeric material.

57. The method of claim 56 wherein the degradable polymeric material is a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(e-caprolactone), a poly(hydroxybutyrate), a poly(anhydride), an aliphatic polycarbonate, an orthoester, a poly(orthoester), a poly(aminoc acid), a poly(ethylene oxide), a polyphosphazene, or a combination thereof.

58. The method of claim 52 wherein the viscosified treatment fluid further comprises a surfactant, a breaker, a bactericide, a crosslinker, a pH control additive, a stabilizer, or a fluid loss control additive.

59. The method of claim 52 wherein the viscosified treatment fluid further comprises a salt.

60. The method of claim 57 wherein the pH control additive comprises a chelating agent, a base, an acid, a combination of a chelating agent and an acid, or a combination of a chelating agent and a base.

61. The method of claim 57 wherein the viscosified treatment fluid further comprises an activator or a retarder.

62. A method of fracturing a portion of a subterranean formation comprising:

- providing a viscosified fracturing fluid comprising a gelling agent that comprises scleroglucan; and
- contacting the portion of the subterranean formation with the viscosified fracturing fluid at a sufficient pressure to create or enhance at least one fracture in the subterranean formation.

63. A method of producing hydrocarbons from a subterranean formation wherein a viscosified treatment fluid comprising a gelling agent that comprises scleroglucan is used in a completion or a servicing operation.

64. A method of producing hydrocarbons from a subterranean formation wherein a viscosified treatment fluid comprising a gelling agent that comprises diutan is used and the subterranean formation has a temperature greater than or equal to 200°F.

65. A method of producing hydrocarbons from a subterranean formation wherein a viscosified treatment fluid comprising a gelling agent that comprises diutan and a breaker that comprises a peroxide are used.

66. A subterranean well treatment system comprising a viscosified treatment fluid that comprises diutan and a breaker that comprises a peroxide breaker.

67. The system of claim 66 wherein the breaker comprises tert-butyl hydroperoxide or tert-amyl hydroperoxide.

68. The system of claim 66 wherein at least a portion of the breaker is encapsulated by a coating.

69. The system of claim 68 wherein the coating comprises a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(e-caprolactone), a poly(hydroxybutyrate), a poly(anhydride), an aliphatic polycarbonate, an orthoester, a poly(orthoester), a poly(aminoc acid), a poly(ethylene oxide), a polyphosphazene, or a combination thereof.

70. The system of claim 66 wherein the breaker is present in an amount sufficient to reduce the viscosity of the viscosified treatment fluid to facilitate the recovery of the fluid.

71. The system of claim 66 wherein the viscosified treatment fluid comprises fresh water, salt water, or a brine.

72. The system of claim 66 wherein the viscosified treatment fluid comprises a monovalent brine.

73. The system of claim 66 wherein the viscosified treatment fluid comprises a salt.

74. The system of claim 66 wherein the viscosified treatment fluid comprises a pH control additive, a surfactant, a bactericide, a crosslinker, a fluid loss control additive, proppant, gravel, or a combination thereof.

75. A subterranean well servicing or completion fluid comprising a gelling agent that comprises scleroglucan.

76. The composition of claim 75 wherein the subterranean well servicing or completion fluid comprises propellant.

77. The composition of claim 75 wherein the subterranean well servicing or completion fluid further comprises a surfactant, a bactericide, a crosslinker, a pH control additive, or a fluid loss control additive.

78. The composition of claim 75 wherein the subterranean well servicing or completion fluid comprises fresh water, salt water, or a brine.

79. The composition of claim 75 wherein the subterranean well treatment fluid further comprises a salt.

80. The composition of claim 79 wherein the salt comprises potassium chloride, sodium bromide, ammonium chloride, cesium formate, potassium formate, sodium formate, sodium nitrate, calcium bromide, zinc bromide, or sodium chloride.

81. The composition of claim 76 wherein the pH control additive comprises a chelating agent, a base, an acid, a combination of a chelating agent and an acid, or a combination of a chelating agent and a base.

82. A method of making a treatment fluid comprising a scleroglucan gelling agent comprising:

- dissolving scleroglucan in water to produce a solution;
- neutralizing the solution from a pH of about 13 to one of a pH of less than about 12 to form a viscosified treatment fluid comprising a scleroglucan gelling agent.

83. The method of claim 82 wherein the water comprises a salt.

84. The method of claim 82 wherein the water has a pH of about 13.

85. A viscosified treatment fluid made by the method of claim 82.