METHODS AND COMPOSITIONS FOR SERVICING FLUIDS COMPRISING DERIVATIZED CELLULOSE GELLING AGENTS

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ABSTRACT

One embodiment of the present invention provides methods of treating a portion of a subterranean formation, comprising providing a treatment fluid comprising a derivatized cellulose gelling agent wherein the derivatized cellulose gelling agent is made by reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid; and, placing the treatment fluid in the portion of the subterranean formation. Another embodiment of the present invention provides methods of derivatizing cellulose, comprising reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid. Another embodiment of the present invention provides crosslinkable treatment fluids for use in subterranean formations comprising a derivatized cellulose gelling agent wherein the derivatized cellulose gelling agent comprises a cellulose that has been derivatized to comprise an alpha carboxylic acid or a compound comprising a 1,3-cis diol moiety.
METHODS AND COMPOSITIONS FOR SERVICING FLUIDS COMPRISING DERIVATIZED CELLULOSE GELLING AGENTS

BACKGROUND OF THE INVENTION

0001 The present invention relates to hydraulic fracturing treatments. More particularly, the present invention relates to methods and compositions for servicing fluids comprising derivatized cellulose gelling agents.

0002 Servicing fluids are used in a variety of operations and treatments performed in oil and gas wells. Such operations and treatments include, but are not limited to, production stimulation operations, such as fracturing, and well completion operations, such as gravel packing and frac packing.

0003 An example of a production stimulation operation using a servicing fluid is hydraulic fracturing. That is, a type of servicing fluid, referred to in the art as a fracturing fluid, is pumped through a well bore into a subterranean zone to be stimulated at a rate and pressure such that fractures are formed or enhanced in a desired subterranean zone. The fracturing fluid is generally a gel, emulsion, or foam that may comprise a particulate material often referred to as proppant. When used, proppant is deposited in the fracture and functions, inter alia, to hold the fracture open while maintaining conductive channels through which such produced fluids can flow upon completion of the fracturing treatment and release of the attendant hydraulic pressure.

0004 An example of a well completion operation using a servicing fluid having particles suspended therein is gravel packing. Gravel packing treatments are used, inter alia, to reduce the migration of unconsolidated formation particulates into the well bore. In gravel packing operations, particulates, referred to in the art as gravel, are carried to a well bore in a subterranean producing zone by a servicing fluid known as a carrier fluid. That is, the particulates are suspended in a carrier fluid, which may be viscosified, and the carrier fluid is pumped into a well bore in which the gravel pack is to be placed. As the particulates are placed in the zone, the carrier fluid leaks off into the subterranean zone and/or is returned to the surface. The resultant gravel pack acts as a filter to separate formation solids from produced fluids while permitting the produced fluids to flow into and through the well bore. While screenless gravel packing operations are becoming more common, traditional gravel pack operations involve placing a gravel pack screen in the well bore and packing the surrounding annulus between the screen and the well bore with gravel designed to prevent the passage of formation particulates through the pack with produced fluids, wherein the well bore may be oriented from vertical to horizontal and may extend from hundreds to thousands of feet. When installing the gravel pack, the gravel is carried to the formation in the form of a slurry by mixing the gravel with a viscosified carrier fluid. Such gravel packs may be used to stabilize a formation while causing minimal impairment to well productivity. The gravel, inter alia, acts to prevent the particulates from occluding the screen or migrating with the produced fluids, and the screen, inter alia, acts to prevent the gravel from entering the well bore.

0005 In some situations the processes of hydraulic fracturing and gravel packing are combined into a single treatment to provide stimulated production and an annular gravel pack to prevent formation sand production. Such treatments are often referred to as “frac pack” operations. In some cases the treatments are completed with a gravel pack screen assembly in place with the hydraulic fracturing treatment being pumped through the annular space between the casing and screen. In this situation the hydraulic fracturing treatment ends in a screen out condition creating an annular gravel pack between the screen and casing. This allows both the hydraulic fracturing treatment and gravel pack to be placed in a single operation. In other cases the fracturing treatment may be performed prior to installing the screen and placing a gravel pack.

0006 A variety of methods are used to create the gelled or emulsified fracturing fluids typically used in subterranean operations. Generally, a polysaccharide or synthetic polymer gelling agent is used to impart viscosity to the servicing fluid to, among other things, enhance proppant transport and reduce fluid loss from the servicing fluid into the formation. Frequently, a crosslinking agent, such as a metallic compound, is also added to further enhance the viscosity of the fluid by coupling, or “crosslinking,” polymer molecules. The fracturing fluid may also include one or more of a variety of well-known additives, such as gel stabilizers, fluid loss control agents, clay stabilizers, bactericides, and the like.

0007 One common gelling agent used in servicing fluids is guar, a galactomannan type of saccharide which can be crosslinked to yield a high gel strength for suspension, and yet can be easily “broken,” or converted to a low viscosity fluid, by breakers in fracturing fluids. Because of its abundance, price, and geometry favorable to crosslinking, guar is the most commonly used gelling agent in servicing fluids. Despite its widespread use, though, guar still suffers from a variety of shortcomings, including its lack of thermal stability and sensitivity to pH and bacterial fermentation.

SUMMARY OF THE INVENTION

0008 The present invention relates to hydraulic fracturing treatments. More particularly, the present invention relates to methods and compositions for servicing fluids comprising derivatized cellulose gelling agents.

0009 One embodiment of the present invention provides methods of treating a portion of a subterranean formation, comprising providing a treatment fluid comprising a derivatized cellulose gelling agent wherein the derivatized cellulose gelling agent is made by reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid; and, placing the treatment fluid in the portion of the subterranean formation.

0010 Another embodiment of the present invention provides methods of derivatizing cellulose, comprising reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid.

0011 Another embodiment of the present invention provides crosslinkable treatment fluids for use in subterranean formations comprising a derivatized cellulose gelling agent wherein the derivatized cellulose gelling agent comprises a cellulose that has been derivatized to comprise an alpha carboxylic acid or a compound comprising a 1,3-cis diol moiety.
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

The present invention relates to hydraulic fracturing treatments. More particularly, the present invention relates to methods and compositions for servicing fluids comprising derivatized cellulose gelling agents.

In accordance with the present invention, cellulose may be derivatized using an electrophilic agent, such as glycidol, such derivatization results in the formation of either an alpha carboxylic acid or a compound having a 1,3-cis diol moiety. The diol geometry is generally favorable to crosslinking, allowing the cellulose to be linked at viscosities comparable to guar but suitable for use over a broader range of temperatures. Similarly, alpha-hydroxy carboxylic acids and derivatives thereof may be attached via ring opening of an oxirane ring followed by hydrolysis to reveal crosslinking groups with favorable geometries. These properties make derivatized cellulose an economical gelling agent suitable for use in a servicing fluid in hydraulic fracturing, frac-packing, and gravel packing applications.

Generally, any known physical form of a servicing fluid suitable for a subterranean operation may be used in accordance with the teachings of the present invention, including aqueous gels, foams, and emulsions. Suitable aqueous gels are generally comprised of water and one or more gelling agents. Suitable emulsions may be comprised of two immiscible liquids such as an aqueous gelled liquid and a liquefied, normally gaseous fluid, such as carbon dioxide. Foams can be prepared by mixing viscous gelled liquids with gases such as nitrogen. In some embodiments of the present invention, all the servicing fluids are aqueous gels comprised of water, a cellulose gelling agent for gelling the water and increasing its viscosity, and a cross-linking agent for cross-linking the gel and further increasing the viscosity of the fluid. The increased viscosity of the gelled, or gelled and cross-linked, fracturing fluid, inter alia, reduces fluid loss and may allow the servicing fluid to transport significant quantities of suspended particulates. The water used to form the servicing fluid may be fresh water, salt water, brine, or any other aqueous liquid that does not adversely react with the other components.

As mentioned above, the fracturing fluids of the present invention comprise at least one derivatized cellulose gelling agent that has been prepared by treating a cellulose with an electrophilic agent to form an alpha carboxylic acid or a compound having a 1,3-cis diol moiety. Any known cellulose may be used in conjunction with the present invention. Suitable derivatized forms of cellulose may be used as well, including, but not limited to, hydroxyethyl cellulose, which is commercially available from Halliburton Energy Services, Inc., of Duncan, Okla., under the trade-name “WG-17™.” Any other cellulose capable of reacting with an electrophilic reagent may also be used in accordance with the teachings of the present invention, including cellulose pulp, cellulose derivatives, and pretreated cellulose.

Due to hydrogen bonding between adjacent cellulose chains, cellulose is typically a tightly wound, high-strength polymer that is insoluble in most solvents, including water. Therefore, particular embodiments of the present invention pre-treat the cellulose with an alkaline solution comprising a denaturing agent capable of breaking inter- and intra-molecular bonds of the cellulose. This solution helps disrupt the hydrogen bonding between the cellulose and increase its solubility. Suitable denaturing agents include, but are not limited to, urea, thiourea, guanidine, and other agents known to disrupt hydrogen bond networks. Other suitable denaturing agents may also be apparent to one skilled in the art with the benefit of this disclosure; by way of example, in some embodiments, ionic liquids (such as tetraethyl ammonium hydroxide) may be used to pre-treat the cellulose.

After any necessary pretreatment with the alkaline solution, the cellulose may be treated with an electrophilic agent. Generally, the electrophilic agent of the present invention may be any electrophilic agent that reacts with cellulose to form an alpha carboxylic acid or a compound having a 1,3-cis diol moiety. Examples of suitable electrophilic agents include, but are not limited to, glycidol (i.e., 1,2-epoxy-1-propanol) glycidyl butyrate, glycidyl 4-nitrobenzoate, glycidyl 3-nitrobenzoate, glycidyl 3-nitrobenzenesulfonate, glycidyl p-toluenesulfonate, glycidyl tosylate, epichlorohydrin, and methyl (2R)-glycidate. Suitable electrophilic agents react with the cellulose to attach a 1,3-dihydroxy group to the cellulose backbone such that the resulting cellulose derivative exhibits a 1,3-cis diol geometry that will accommodate the ligand sphere of an appropriate crosslinker and thus allow the derivatized cellulose to be crosslinked and suitable for use in a fracturing fluid such as a fracturing fluid.

Preparation of a cellulose having a 1,3-cis diol moiety may be accomplished via a ring opening alkylation using a commercially available lactone such as alpha-hydroxy-gamma butyrolactone. One skilled in the art would recognize the alpha carboxylic acids could be prepared via a number of routes. By way of example, one example of a method for preparing an alpha carboxylic acid derivative involves adding 100 g of Alpha Cell BH200 (a fine white powder cellulose having a particle size defined by the following: on 40 mesh screen less than 0.5%, through 100-Mesh screen, not less than 90%; and through 200 mesh screen, not less than 75%) purchased from IFC of North Tonawanda, N.Y. to a concentrated brine solution containing 5% by weight potassium hydroxide and 8% by weight potassium chloride in 60 grams of distilled water and then stirring the mixture under a nitrogen purge and then adding 10% by weight glycidol and then stirring at room temperature for 12 hours to create a crosslinkable cellulose derivative evidenced by the gelation of the polymer through the addition of boron. Also, by way of example, another method for preparing an alpha carboxylic acid derivative involves adding 100 g of Alpha Cell BH200 to 500 mL of tetraethyl ammonium hydroxide (to dissolve the cellulose) and then stirring the mixture at an elevated temperature (about 150°F.) for twelve hours; the resulting polymer was shown to be able to crosslink in the presence of a boronic acid crosslinker.

Such derivatized cellulose may then be crosslinked using known crosslinking agents. Examples of suitable crosslinking agents include compounds that are capable of releasing multivalent metal ions. Examples of multivalent metal ions in suitable crosslinking agents include boron,
chromium, zirconium, antimony, calcium, magnesium, titanium, iron, zinc, or aluminum. When used, the crosslinking agent is generally added to the gelled water in an amount in the range of from about 0.01% to about 5% by weight of the water, preferably 0.01% to about 2% by weight of the polymer. One skilled in the art will recognize that suitable crosslinking agents may contain at little as 2% or as much as 15% or more of the metal component that acts as the active portion of the crosslinker.

[0021] The gelled or gelled and cross-linked fracturing fluids may also include internal delayed gel breakers such as enzyme, oxidizing, acid buffer, or temperature-activated gel breakers. The gel breakers cause the viscous carrier fluids, inter alia, to revert to thin fluids that can be produced back to the surface after they have been used to place proppant particles in subterranean fractures. The gel breaker used is typically present in the fracturing fluid in an amount in the range of from about 1% to about 5% by weight of the gelling agent. The fracturing fluids may also include one or more of a variety of well-known additives, such as gel stabilizers, fluid loss control additives, clay stabilizers, bactericides, and the like.

[0022] Generally, the crosslinked fluids of the present invention are suitable for use in hydraulic fracturing, frac-packing, and gravel packing applications. In exemplary embodiments of the present invention where the crosslinked fluids are used to carry proppant, the proppant is generally of a size such that formation fines that may migrate with the produced fluids are prevented from being produced from the subterranean zone. Any suitable particulate may be used, including graded sand, bauxite, ceramic materials, glass materials, walnut hulls, polymer beads, and the like. Generally, the proppant has a size in the range of from about 4 to about 400 mesh, U.S. Sieve Series. In some embodiments of the present invention, the proppant is graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series. In particular embodiments of the present invention, the proppant may be at least partially coated with a curable resin, tackifying agents, or some other flowback control agent or formation fine control agent.

[0023] Therefore, the present invention is well adapted to 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:
   providing a treatment fluid comprising a derivatized cellulose gelling agent wherein the derivatized cellulose gelling agent is made by reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid; and,
   placing the treatment fluid in the portion of the subterranean formation.

2. The method of claim 1 wherein the gelling agent is produced by reacting an electrophilic agent with cellulose to attach at least one 1,3-dihydroxy group to the cellulose.

3. The method of claim 2 wherein the electrophilic agent comprises glycidol or epichlorohydrin.

4. The method of claim 2 wherein, before reacting the electrophilic agent with the cellulose, the cellulose is pretreated with an alkaline solution that comprises at least one of the following: urea, thiourea, or guanidine.

5. The method of claim 1 wherein the treatment fluid further comprises a metallic crosslinking agent and wherein the metallic crosslinking agent comprises at least one of the following: boron, chromium, zirconium, antimony, calcium, magnesium, titanium, iron, zinc, or aluminum.

6. The method of claim 1 wherein the treatment fluid further comprises at least one of the following: a gel stabilizer, breaker, fluid loss control agent, surfactant, clay stabilizer, bactericide, or proppant.

7. The method of claim 6 wherein the proppant is at least partially coated with a either a curable resin or a tackifying agent.

8. A method of derivatizing cellulose, comprising reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid.

9. The method of claim 8 wherein the electrophilic agent comprises glycidol or epichlorohydrin.

10. The method of claim 8 wherein the electrophilic agent attaches at least one 1,3-dihydroxy group to the cellulose.

11. The method of claim 8 further comprising at least partially dissolving the cellulose in an alkaline solution prior to reacting the cellulose with the electrophilic agent.

12. The method of claim 11 wherein the alkaline solution comprises at least one of the following: urea, thiourea, or guanidine.

13. The method of claim 8 further comprising, after reacting cellulose with an electrophilic agent, exposing the cellulose to a metallic crosslinking agent wherein the metallic crosslinking agent comprises at least one of the following: boron, chromium, zirconium, antimony, calcium, magnesium, titanium, iron, zinc, or aluminum.

14. A crosslinkable treatment fluid for use in subterranean formations comprising a derivatized cellulose gelling agent wherein the derivatized cellulose gelling agent is made by reacting cellulose with an electrophilic agent to form a 1,3-cis diol or an alpha carboxylic acid.

15. The crosslinkable treatment fluid of claim 14 wherein the derivatized cellulose gelling agent is produced by reacting an electrophilic agent with cellulose to attach at least one 1,3-dihydroxy group to the cellulose.

16. The crosslinkable treatment fluid of claim 15 wherein the electrophilic agent comprises glycidol or epichlorohydrin.

17. The crosslinkable treatment fluid of claim 15 wherein the cellulose is pretreated with an alkaline solution before the cellulose is derivatized and wherein the alkaline solution comprises at least one of the following: urea, thiourea, or guanidine.

18. The crosslinkable treatment fluid of claim 14 further comprising a metallic crosslinking agent and wherein the metallic crosslinking agent comprises at least one of the following: boron, chromium, zirconium, antimony, calcium, magnesium, titanium, iron, zinc, or aluminum.

19. The crosslinkable treatment fluid of claim 14 further comprising a gel stabilizer, breaker, fluid loss control agent, surfactant, clay stabilizer, bactericide, or proppant.

20. The crosslinkable treatment fluid of claim 19 wherein the proppant is at least partially coated with either a curable resin or a tackifying agent.

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