METHODS OF MAKING AND USING SULFONATED OR CARBOXYLATED POLYSACCHARIDE GELLING AGENTS

One embodiment of the present invention provides a method of treating a subterranean formation comprising: providing a treatment fluid comprising a sulfonated polysaccharide gelling agent wherein the sulfonated polysaccharide gelling agent is produced by reacting a cyclic sulfone with a polysaccharide; and, introducing the treatment fluid into a portion of a subterranean formation. Another embodiment provides a method of treating a subterranean formation, comprising: providing a treatment fluid comprising a carboxylated polysaccharide gelling agent wherein the carboxylated polysaccharide gelling agent is produced by reacting a polysaccharide with at least one of the following: a cyclic lactone or a cyclic phosphonate acid; and introducing the treatment fluid into a portion of a subterranean formation. Another embodiment provides a method of derivatizing a polysaccharide comprising reacting a polysaccharide with at least one of the following: a cyclic sulfone, a cyclic lactone, or a cyclic phosphonate acid.
METHODS OF MAKING AND USING SULFONATED OR CARBOXYLATED POLYSACCHARIDE GELLING AGENTS

BACKGROUND OF THE INVENTION

The present invention relates to subterranean treatment fluids comprising sulfonated or carboxylated polysaccharide gelling agents and methods of using such treatment fluids.

Treatment fluids are used in a variety of operations performed in oil and gas wells, including production stimulation operations (such as fracturing) and well completion operations (such as gravel packing). An example of a production stimulation operation using a treatment fluid is hydraulic fracturing. That is, a type of treatment 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 produced fluids can flow upon completion of the fracturing treatment and release of the attendant hydraulic pressure.

An example of a well completion operation using a treatment fluid 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 portion of a well bore by a treatment fluid. That is, the particulates are suspended in a treatment fluid, which may be viscosified, and the treatment 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 treatment 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.
In some situations the processes of hydraulic fracturing and gravel packing are combined into a single treatment to provide both stimulated production and an annular gravel pack. 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.

A variety of methods are used to create the viscosified treatment fluids typically used in subterranean operation. Generally, a polysaccharide or synthetic polymer gelling agent is used to impart viscosity to the treatment fluid to, among other things, enhance particulate transport and reduce fluid loss from the treatment fluid into the formation. Frequently, a crosslinking agent, such as a metallic compound, is also added to further enhance the viscosity of the treatment fluid by coupling, or “crosslinking,” gelling agent molecules. One class of gelling agents employed in hydrocarbon production is sulfonated and carboxylated polysaccharides, which provide unique properties for crosslinking at higher temperatures and tolerate higher brine concentrations in source waters. Previous sulfonation or carboxylation processes typically involved reacting polysaccharides with alkyl halides and pendant sulfonates or carboxylates, respectively, under alkaline aqueous conditions. However, these reactions have been inhibited by the fact that pendant sulfonates or carboxylates decompose under aqueous conditions, often before they react with the polysaccharides. Hence, the sulfonation or carboxylation reactions suffered from low yields, low degrees of substitution, and a lack of consistency in reaction products from batch to batch. These problems limit the commercial viability of sulfonated or carboxylated gelling agents in treatment fluids.

**SUMMARY OF THE INVENTION**

The present invention relates to subterranean treatment fluids comprising sulfonated or carboxylated polysaccharide gelling agents and methods of using such treatment fluids.

One embodiment of the present invention provides a method of treating a subterranean formation comprising: providing a treatment fluid comprising a sulfonated polysaccharide gelling agent wherein the sulfonated polysaccharide gelling agent is produced
by reacting a cyclic sultone with a polysaccharide; and, introducing the treatment fluid into a portion of a subterranean formation.

Another embodiment of the present invention provides a method of treating a subterranean formation, comprising: providing a treatment fluid comprising a carboxylated polysaccharide gelling agent wherein the carboxylated polysaccharide gelling agent is produced by reacting a polysaccharide with at least one of the following: a cyclic lactone or a cyclic phosphonate acid; and introducing the treatment fluid into a portion of a subterranean formation.

Another embodiment of the present invention provides a method of derivatizing a polysaccharide comprising reacting a polysaccharide with at least one of the following: a cyclic sultone, a cyclic lactone, or a cyclic phosphonate acid.

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.

**BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 shows the results of a $^{13}$C NMR DEPT spectroscopy test run on a sulfonated gelling agent of the present invention.

**DESCRIPTION OF PREFERRED EMBODIMENTS**

The present invention relates to subterranean treatment fluids comprising sulfonated or carboxylated polysaccharide gelling agents and methods of using such treatment fluids.

In accordance with the present invention, a sulfonated or carboxylated polysaccharide gelling agent may be used to increase the viscosity of a treatment fluid. Generally, these gelling agents are produced by reacting a polysaccharide with a cyclic sultone or lactone, respectively, in a ring-opening reaction to sulfonate or carboxylate the polysaccharide. Such sulfonated or carboxylated polysaccharides may be crosslinked at higher temperatures and may tolerate higher brine levels than their non-sulfonated or non-carboxylated counterparts and thus they are useful in a variety of treatment fluids. Furthermore, sulfonation and carboxylation via ring-opening reactions may offer greater yields and higher degrees of substitution that previous sulfonation or carboxylation methods.

Generally, any form of an aqueous treatment fluid suitable for a use in a subterranean operation such as fracturing or gravel packing 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. The emulsions can be
comprised of two immiscible liquids such as an aqueous gelled liquid and a liquefied, normally gaseous fluid, such as nitrogen. In exemplary embodiments of the present invention, the treatment fluids are aqueous gels comprised of water, a sulfonated or carboxylated gelling agent for gelling the water and increasing its viscosity, and, optionally, a crosslinking agent for crosslinking the gelling agent and further increasing the viscosity of the fluid. The increased viscosity of the gelled, or gelled and crosslinked, treatment fluid, *inter alia*, reduces fluid loss and may allow the treatment fluid to transport significant quantities of suspended particulates. The water used to form the treatment fluid may be fresh water, sea water, salt water, brine, or any other aqueous liquid that does not adversely react with the other components (such as the gelling agent or crosslinking agent).

Any gelling agent that is capable of being sulfonated or carboxylated may be used in accordance with the present invention, including hydratable polymers that contain one or more functional groups such as hydroxyl, carboxyl, sulfate, sulfonate, amino, or amide groups. The gelling agent may be a hydrated guar split, a guar flour, a cellulose pulp, or any polysaccharide. Suitable materials may range from relatively raw materials, such as a guar splits, to processed materials such as derivatized guar flours. Particularly useful are polysaccharides that contain one or more of the monosaccharide units such as galactose, mannose, glucoside, glucose, xylose, arabinose, fructose, glucuronic acid, or pyranosyl sulfate. Examples of natural hydratable polymers containing the foregoing functional groups and units that are suitable for use in accordance with the present invention include, but are not limited to, guar, guar derivatives, hydroxypropyl guar, carboxymethyl guar, xanthan, chitosan, scleroglucan, succinoglycan, starch, biopolymers, cellulose, cellulose derivatives, and hydroxyethyl cellulose. Hydratable synthetic polymers and copolymers that contain the above-mentioned functional groups (*e.g.*, hydroxyl, carboxyl, sulfate, sulfonate, amino, or amide groups) may also be used. Examples of such synthetic polymers include, but are not limited to, acrylamido-methyl-propane sulfonate ("AMPS"), polyacrylate, polymethacrylate, polyacrylamide, polyvinyl alcohol, and polyvinylpyrrolidone. With the benefit of this disclosure, it should be within the ability of one skilled in the art to select an appropriate gelling agent for use in accordance with the present invention. Particularly preferred gelling agents include guars, guar derivatives, and natural polysaccharides.

As mentioned above, the gelling agents of the present invention are either sulfonated or carboxylated. This allows the gelling agents to exhibit unique properties for crosslinking
at higher temperatures and tolerating higher levels of brine in the subterranean formation. Furthermore, the ring-opening sulfonation and carboxylation reactions offer higher yields and more consistent degrees of substitution than previous sulfonation or carboxylation methods.

In particular embodiments of the present invention where the gelling agents are sulfonated, the polysaccharide gelling agents may be prepared by sulfonating a polysaccharide with a cyclic sultone or a derivative of a cyclic sultone. Generally, these reactions involve an entropically-favored, single-step, ring-opening reaction with a sultone. Suitable sultones include, but are not limited to, 1,3-propyl sultone, 1,4-butyl sultone, and derivatives thereof.

In other embodiments of the present invention, where the gelling agents are carboxylated, the polysaccharide gelling agents may be prepared by carboxylating the polysaccharides with a cyclic lactone or a derivative of a cyclic lactone. Similar to the sulfonation reactions mentioned above, these reactions typically involve an entropically-favored, single-step, ring-opening reaction with a lactone in place of the sultone. Suitable lactones include, but are not limited to, butyrolactone, β-propiolactone, and derivatives thereof.

In other embodiments of the present invention, where the gelling agents are carboxylated, the polysaccharide gelling agents may be prepared by carboxylating the polysaccharides with a cyclic phosphonate acid or a derivative of a cyclic phosphonate acid. Similar to the sulfonation reactions mentioned above, these reactions typically involve an entropically-favored, single-step, ring-opening reaction with a cyclic phosphonate acid or a derivative of a cyclic phosphonate acid in place of the sultone. Suitable cyclic phosphonate acids and derivatives include, but are not limited to, 1,2-oxaphospholane, phosphonate ester, or derivatives of cyclic phosphonic acids.

Generally, the sulfonation and carboxylation reactions may be performed under alkaline conditions, in either an aqueous or a solid phase. As used herein, references to reaction done in the “solid phase” refer to reactions with a polymer that has not been previously dissolved. The polymer may be hydrated to achieve a solution phase reaction. Once in the presence of alkaline caustic agents, a sultone or lactone may be added, then heated to achieve a sulfonation or carboxylation reaction, respectively. Once sulfonated or carboxylated, the chosen gelling agent is generally combined with the water to create a treatment fluid. In some embodiments the sulfonated or carboxylated gelling agent is present
in the treatment fluid in an amount in the range of from about 0.01% to about 3% by weight of the water. In some embodiments the sulfonated or carboxylated gelling agent is present in the treatment fluid in an amount in the range of from about 0.01% to about 2% by weight of the water.

In particular embodiments, the treatment fluids of the present invention may also include a crosslinking agent. Crosslinking agents typically comprise at least one ion that is capable of crosslinking at least two gelling agent molecules. Examples of suitable crosslinking agents include, but are not limited to, N,N'-methylenebisacrylamide, boric acid, disodium octaborate tetrahydrate, sodium diborate, pentaborates, ulexite and colemanite, compounds that can supply zirconium IV ions (such as, for example, zirconium lactate, zirconium lactate triethanolamine, zirconium carbonate, zirconium acetylacetonate, zirconium malate, zirconium citrate, and zirconium diisopropylamine lactate); compounds that can supply titanium IV ions (such as, for example, titanium lactate, titanium malate, titanium citrate, titanium ammonium lactate, titanium triethanolamine, and titanium acetylacetonate); aluminum compounds (such as, for example, aluminum lactate or aluminum citrate); antimony compounds; chromium compounds; iron compounds; copper compounds; zinc compounds; or a combination thereof. An example of a suitable commercially available zirconium-based crosslinker is “CL-24” available from Halliburton Energy Services, Inc., Duncan, Oklahoma. An example of a suitable commercially available titanium-based crosslinking agent is “CL-39” available from Halliburton Energy Services, Inc., Duncan Oklahoma. Suitable crosslinking agents generally are present in the viscosified treatment fluids of the present invention in an amount sufficient to provide, inter alia, the desired degree of crosslinking between gelling agent molecules. In some embodiments of the present invention, the crosslinking agent may be present in an amount in the range from about 0.001% to about 10% by weight of the water in the treatment fluid. In some embodiments of the present invention, the crosslinking agent may be present in an amount in the range from about 0.01% to about 1% by weight of the water in the treatment fluid. Individuals skilled in the art, with the benefit of this disclosure, will recognize the exact type and amount of crosslinker to use depending on factors such as the specific gelling agent, desired viscosity, and formation conditions.

The gelled or gelled and crosslinked treatment 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 treatment fluids to revert to relatively thin fluids that can be produced back to the surface after they have been used to, for example, place particulates in subterranean fractures. The gel breaker used is typically present in the servicing fluid in an amount in the range of from about 1% to about 5% by weight of the gelling agent. The servicing 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.

Generally, the treatment 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 treatment fluids are used to carry particulates, the particulates are generally of a size such that formation fines that may migrate with 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 particulates have 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 particulates are 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 particulates may be at least partially coated with a curable resin, tackifying agents, or some other flowback control agent or formation fine control agent.

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

EXAMPLES

Figure 1 and Table 1 show the results of an experiment wherein a polysaccharide (guar) was subjected to a ring-opening reaction under alkaline conditions to sulfonate the polysaccharide. Initially, a control was prepared by adding 100 g guar bean splits to 60 g of water at 140°F followed by 10 g of potassium chloride and 15 g of sodium hydroxide. Another sample was identically prepared and then an additional 5 g of 1,3 propane sultone was added to the second sample. Each sample was dried in a roller oven for 2 hours at 150°F in an oxygen-free environment. After grinding and dehydration, the samples were sieved and tested for covalent attachment of the sultone.
To verify the sultone was covalently attached, the powder was subjected to extraction with dichloromethane using a Soxhlet apparatus. Evaporation and analysis of the extract demonstrated that the sultone was not present. Next, characterization by $^{13}$C NMR DEPT spectroscopy unambiguously identified attachment of the sultone onto the powder. The DEPT experiment distinguishes between methyl (CH3), methylene (CH2) and methine (CH) carbons by showing the opposite phase signal for the methylene as opposed to the methyl and methine carbons. Successful attachment of the sultone is demonstrated unambiguously by the identification of three new methylene peaks shown in Figure 1. The common methylene signal as expected is from the native and derivatized guar. The methylene peaks demonstrate the attachment of a sultone functional group to the guar.

To further characterize the differences between the derivatized and underivatized guar powders, a hydration test was run by measuring the change in viscosity with time. A concentration of 40 pounds per thousand gallons concentration was prepared for each gelling agent in tap water containing 2% (wt/wt) KCl. The change in viscosity with time was measured using a Fann 35 viscometer and the results are presented in Table 1. The difference in base gel viscosities from otherwise identical samples demonstrates the change in physical property from the derivitization of the polymer.

<table>
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<th>Time (min)</th>
<th>Visc cP Control</th>
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<tr>
<td>2</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>16.8</td>
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<td>60</td>
<td>25.9</td>
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</tr>
<tr>
<td>120</td>
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<td>32.5</td>
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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 subterranean formation comprising:
   providing a treatment fluid comprising a sulfonated polysaccharide gelling agent
   wherein the sulfonated polysaccharide gelling agent is produced by reacting a cyclic sultone
   with a polysaccharide; and,
   introducing the treatment fluid into a portion of a subterranean formation.

2. The method of claim 1 wherein the cyclic sultone comprises at least one of the
   following: 1,3-propylsultone, 1,4-butylsultone, a derivative of 1,3-propylsultone, a derivative
   of 1,4-butylsultone, or a derivative of a cyclic sultone.

3. The method of claim 1 wherein the cyclic sultone and polysaccharide are
   reacted under alkaline solid phase conditions.

4. The method of claim 1 wherein the cyclic sultone and polysaccharide are
   reacted under alkaline aqueous conditions.

5. The method of claim 1 wherein the treatment fluid further comprises a
   crosslinking agent and wherein the crosslinking agent comprises at least one of: N,N'-
   methylenbisacrylamide, boric acid, disodium octaborate tetrahydrate, sodium diborate, a
   pentaborate, ulexite, colemanite, a compound that can supply zirconium IV ions, a compound
   that can supply titanium IV ions, an aluminum compound, an antimony compound; a
   chromium compound; an iron compound; a copper compound; or a zinc compound.

6. The method of claim 1 wherein the treatment fluid further comprises a gel
   stabilizer, gel breaker, fluid loss control additive, clay stabilizer, or bactericide.

7. The method of claim 1 wherein the treatment fluid further comprises
   particulates.

8. A method of treating a subterranean formation, comprising:
   providing a treatment fluid comprising a carboxylated polysaccharide gelling agent
   wherein the carboxylated polysaccharide gelling agent is produced by reacting a
   polysaccharide with at least one of the following: a cyclic lactone or a cyclic phosphonate
   acid; and
   introducing the treatment fluid into a portion of a subterranean formation.

9. The method of claim 8 wherein the cyclic lactone comprises butyrolactone, 1
   -propiolactone, a derivative of butyrolactone, a derivative of 1-propiolactone, or a derivative
   of a cyclic lactone.
10. The method of claim 8 wherein the cyclic phosphonate acid comprises 1,2-oxaphospholane, a phosphonate ester, or a derivative of a cyclic phosphonic acid.

11. The method of claim 8 wherein the cyclic lactone and polysaccharide are reacted under alkaline solid phase conditions.

12. The method of claim 8 wherein the cyclic lactone and polysaccharide are reacted under alkaline aqueous conditions.

13. The method of claim 8 wherein the treatment fluid further comprises a crosslinking agent and wherein the crosslinking agent comprises at least one of: N,N'-methylenebisacrylamide, boric acid, disodium octaborate tetrahydrate, sodium diborate, a pentaborate, ulexite, colemante, a compound that can supply zirconium IV ions, a compound that can supply titanium IV ions, an aluminum compound, an antimony compound; a chromium compound; an iron compound; a copper compound; or a zinc compound.

14. The method of claim 8 wherein the treatment fluid further comprises a gel stabilizer, gel breaker, fluid loss control additive, clay stabilizer, or bactericide.

15. The method of claim 8 wherein the treatment fluid further comprises particulates.

16. A method of derivatizing a polysaccharide comprising reacting a polysaccharide with at least one of the following: a cyclic sultone, a cyclic lactone, or a cyclic phosphonate acid.

17. The method of claim 16 wherein the cyclic sultone comprises at least one of the following: 1,3-propylsultone, 1,4-butylsultone, a derivative of 1,3-propylsultone, a derivative of 1,4-butylsultone, or a derivative of a cyclic sultone.

18. The method of claim 16 wherein the cyclic lactone comprises butyrolactone, β-propiolactone, a derivative of butyrolactone, a derivative of β-propiolactone, or a derivative of a cyclic lactone.

19. The method of claim 16 wherein the cyclic phosphonate acid comprises 1,2-oxaphospholane, a phosphonate ester, or a derivative of a cyclic phosphonic acid.

20. The method of claim 16 wherein the reaction occurs under either alkaline solid phase conditions or alkaline aqueous conditions.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C09K8/68 C09K8/60

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

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 practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of Box C. See patent family overview.

**Special categories of cited documents:**

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *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)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- **I** 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
- **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
- **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
- **A** document member of the same patent family

**Date of the initial completion of the international search**

27 April 2006

**Date of mailing of the international search report**

08/05/2006

Name and mailing address of the ISA/Authorized officer

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Fax: (+31-70) 340-3016

Zimpfer, E
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