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(54) **METHODES ET COMPOSITIONS POUR RETARDER LA
RETICULATION DE MATERIAUX DE PERTES DE
CIRCULATION, A BASE DE SACCHARIDES**

(54) **METHODS AND COMPOSITIONS FOR DELAYING THE
CROSSLINKING OF CROSSLINKABLE
POLYSACCHARIDE-BASED LOST CIRCULATION
MATERIALS**

(57) On peut fermer de manière étanche des fractures et des formations souterraines perméables, au moyen de fluides de pertes de circulation comprenant des gels de polysaccharide réticulé métallique et de borate, gels qui sont réticulés dans le puits de forage. L'invention concerne des compositions et des procédés permettant de mélanger des solides de matériau de pertes de circulation, dans une cuve de mélangeage, à la surface, avec un polysaccharide réticulable et un agent de réticulation, dans des conditions dans lesquelles le fluide de matériau de pertes de circulation peut être envoyé par pompage dans le puits, avant sa gélification. Une fois le fluide de matériau de pertes de circulation équilibré par rapport à la température du réservoir, le composant polysaccharide du fluide de matériau de perte de circulation se transforme par réticulation.

(57) Permeable subterranean underground formations and fractures can be sealed using lost circulating material fluids having borate and metallic cross-linked polysaccharide gels that are cross-linked in the well bore. Compositions and methods are illustrated whereby lost circulation material solids can be mixed in a mixing tank on the surface with a cross-linkable polysaccharide and a cross-linking agent under conditions whereby the lost circulating material fluid can be pumped into the well bore before undergoing gelation. Once the lost circulation material fluid equilibrates to the reservoir temperature the polysaccharide component of the lost circulation material fluid will cross-link.

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(21) International Application Number: PCT/US99/07740 (22) International Filing Date: 14 April 1999 (14.04.99) (30) Priority Data: 60/081,700 14 April 1998 (14.04.98) US 09/290,799 13 April 1999 (13.04.99) US (71) Applicant (for all designated States except US): HALLIBURTON ENERGY SERVICES, INC. [US/US]; 4100 Clinton Drive, Houston, TX 77020 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): DONALDSON, Ashley [-/US]; Houston, TX (US). LAWSON, Jim [-/US]; Houston, TX (US). POWER, David [-/US]; Duncan, OK (US). NORMAN, Lewis, R. [-/US]; Duncan, OK (US). (74) Agents: TRIPP, Karen, B. et al.; Suite 2690, 1100 Louisiana, Houston, TX 77002 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHODS AND COMPOSITIONS FOR DELAYING THE CROSSLINKING OF CROSSLINKABLE POLYSACCHARIDE-BASED LOST CIRCULATION MATERIALS (57) Abstract <p>Permeable subterranean underground formations and fractures can be sealed using lost circulating material fluids having borate and metallic cross-linked polysaccharide gels that are cross-linked in the well bore. Compositions and methods are illustrated whereby lost circulation material solids can be mixed in a mixing tank on the surface with a cross-linkable polysaccharide and a cross-linking agent under conditions whereby the lost circulating material fluid can be pumped into the well bore before undergoing gelation. Once the lost circulation material fluid equilibrates to the reservoir temperature the polysaccharide component of the lost circulation material fluid will cross-link.</p>		

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**METHODS AND COMPOSITIONS FOR DELAYING
THE CROSSLINKING OF CROSSLINKABLE
POLYSACCHARIDE-BASED LOST CIRCULATION MATERIALS**

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RELATED APPLICATION

This application claims priority to United States Provisional Application Serial No. 60/081,700 filed April 14, 1998.

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BRIEF DESCRIPTION OF THE INVENTION

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The present invention relates in general to methods and compositions for controlling the gelation time of polysaccharide-based fluids used to support and supplement lost circulation materials. The present invention, in particular, relates to methods and compositions for delaying the crosslinking of polysaccharides such as galactomannans with borate and metallic crosslinking agents at ambient temperatures while rapidly crosslinking the polysaccharides at elevated temperatures of about 110°F or higher.

BACKGROUND OF THE INVENTION

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Drillers often encounter zones that accept large volumes of drilling mud. Such losses may occur due to induced hydraulic fractures, open natural fractures, vuggy carbonate, or coarse sand and gravel. To control severe mud losses, operators circulate high concentrations of sized solids suspended in viscous fluids, or gels. Such mixtures are referred to as lost circulation material fluids (LCM fluids).

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The purposes of LCM fluids are to bridge and seal very permeable formations and to prevent fractures from growing. Various water-soluble polymers have been used as viscosifiers to assist in the suspension of the lost circulation material solids (LCMs). Galactomannan polymers, such as guar or derivatized guar, are widely used viscosifiers. Gels of galactomannan polymers have excellent solids suspending properties. In addition, these gels can, themselves, serve to bridge and seal vugs and natural fractures.

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Crosslinking agents such as aluminum, antimony, zirconium, titanium and boron containing compounds are employed to crosslink galactomannan polymers to increase the viscosity and gel strength of the LCM fluids and hereinafter the crosslinked LCM fluids are simply referred to as gels. The crosslinking of guar, or hydroxypropyl guar, solutions with these crosslinking agents is pH dependent. For example, gels made from borate crosslinked guar are stable only at pHs greater than about 8.5. At lower pHs they revert to polymeric solutions.

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Consequently, a borate gel can easily be broken to prevent damage to the formation and to gravel packs and slotted liners.

A major disadvantage with respect to mixing of borate crosslinked galactomannans is that at alkaline pHs, pHs greater than a pH of about 8.5, galactomannans crosslink almost
5 instantaneously as an operator adds borate ion. Thus, if the borate is added to the other LCM fluid components in the surface tank at an alkaline pH, the mixture will gel and cannot be pumped from the tank. In addition, large amounts of energy would be required to pump the gel through the well tubing.

One solution is to mix all of the LCM fluid components, except the crosslinking agent
10 at the surface and then inject the crosslinker downstream of the circulating pump. However, such an approach requires additional equipment and tankage. It is also possible to delay crosslinking by waiting to raise the solution pH until the crosslinkable polymer is on its way down the hole. However, this approach also requires extra pumps and tankage.

A need exists for a simple process whereby one can mix all LCM fluid components on the
15 surface in a mixing tank and delay the gelation or crosslinking of those components until after the LCM fluid has been pumped through the drill pipe. Such a process should not require the close monitoring of mixing conditions or timing.

SUMMARY OF THE INVENTION

The invention contemplates preparing a fluid (LCM fluid) to support and supplement lost
20 circulation material solids comprising a solution containing a crosslinkable polysaccharide and a crosslinking agent in a surface tank. Once all of the LCM fluid components are mixed in the surface tank, the fluid is pumped into the well bore where it undergoes an increase in temperature as it proceeds deeper into the well. With increasing time and temperature, the delayed crosslinker
25 reacts with the galactomannan gum thereby yielding a crosslinked fluid with the aforementioned desirable properties.

In accordance with one aspect of the invention, a system for mixing and pumping an
ungelled LCM fluid into a wellbore is provided. The LCM fluid comprises a crosslinkable
polymeric solution and a crosslinking agent, at concentrations and at a pH that will induce
30 crosslinking and gelation of the LCM fluid at temperatures above about 110°F. Preferred crosslinking agents are slowly soluble borate, and delayed reacting organic zirconate or organic titanate.

The foregoing has outlined rather broadly aspects of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features

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and advantages of the lost circulation materials solutions will be described hereinafter which form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the concept and the specific embodiment disclosed may be readily utilized as a basis for modifying or designing other processes or compositions for carrying out the same purpose of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a simple, inexpensive means of preparing fluids used to support lost circulation material solids (LCMs) that will delay the crosslinking of the polymer in the fluid until the LCM fluid has been pumped into the well bore.

The delayed crosslinking LCM fluid contains a number of ingredients, such as a crosslinkable polymer like galactomannan, a crosslinking agent, bridging solids suspended in the LCM fluid, water, a base and/or buffers for adjusting the pH of the LCM fluid, and additional optional components such as gel breakers, weighting material and environmentally friendly esters such as those described in U.S. Patent No. 5,252,554.

One advantage of the described process for mixing LCM fluid components on the surface is that the crosslinking of the LCM fluid components is delayed until after the LCM fluid components have been pumped through the drill pipe. Another advantage of the described process is that the gels used to suspend LCMs do not require any special solution rheology. Since the gels are used to carry solids and bridge and seal vugs and fractures, there is little danger of over-crosslinking the LCM fluid.

The crosslinkable polymer used in the present invention is a high molecular weight water-soluble polysaccharide such as galactomannan. The preferred polysaccharides for the practice of this invention are guar and its derivatives at concentrations varying from about 0.2 to about 1.5 wt.% of the LCM fluid. Specifically, these include guar gum, locust bean gum, karaya gum, carboxymethyl guar, hydroxyethyl guar, carboxymethyl hydroxyethyl guar, hydroxypropyl guar, carboxymethyl hydroxypropyl guar, and mixtures thereof. Guar is a naturally occurring polysaccharide composed of a mannose backbone with galactose side groups. Guar and its derivatives contain cis-hydroxyl groups, which can complex with crosslinking agents such as borate, zirconate and titanate.

A variety of crosslinking agents such as aluminum, antimony, zirconium, titanium and boron containing compounds are suitable for the LCM fluid of the present invention. Preferred embodiments of the invention use borate, zirconate, or titanate crosslinking agents as described

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further below.

1. **Borate Crosslinking Agents**

The source of borate used as the crosslinking agent in the present invention is a slowly soluble borate such as an alkaline earth metal borate, an alkali metal borate, and mixtures thereof. Preferred examples of slowly soluble borate sources are anhydrous sodium tetraborate and ulexite ($\text{NaCaB}_5\text{O}_6 \cdot 5\text{H}_2\text{O}$).

For consistency, ulexite, obtained from Ward's Natural Science Establishment, Inc. or American Borate Company, was ground and particles selected that were smaller than 20 mesh (having an opening of 841 microns) and larger than 40 mesh (having an opening of 420 microns) and used in the examples described below. Similarly particulated anhydrous sodium tetraborate, obtained from U.S. Borax, Inc., was used. The anhydrous sodium tetraborate particles were smaller than 12 mesh, passing through screen openings of 1680 microns, with 90% of the anhydrous sodium tetraborate particles retained by a 70 mesh screen having openings of 297 microns.

Since the crosslinking of the polysaccharide solutions is dependent on the borate ion concentration, the slow solubility of the anhydrous sodium tetraborate and ulexite, as compared to Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), delayed the crosslinking of hydroxypropyl guar (HPG) solutions as seen in Example 1 below. However, rates of dissolution of anhydrous sodium tetraborate and ulexite increased with increased temperatures, thereby raising the borate ion concentration and inducing the crosslinking of the HPG solution. See Example 2.

This factor can be utilized to provide a significant advantage in the field application of borate crosslinked LCM fluids. By taking advantage of this temperature dependence on the rate of dissolution of the slowly soluble borate, all of the LCM fluid components can be mixed in the same tank on the surface and pumped into the well bore. Once the LCM fluid reaches the reservoir and is heated to reservoir temperatures, the borate ion concentration is increased and the polysaccharide crosslinks.

The borate ion concentration of a borate solution is pH dependent. The ionization of borate is almost complete at pH 11 and ambient temperature. The ionization of borate decreases as the pH varies from pH 11, thereby requiring a greater concentration of borate to achieve the necessary borate ion concentration for crosslinking the polysaccharide molecules. In the present invention, the borate ion concentration increases more rapidly with the increased temperature of the well bore, thereby creating the proper conditions to ensure crosslinking of the guar solutions. The gelation time is a function of temperature, pH, and the concentration of borate ion.

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The invention is further defined by reference to the following examples, which are intended to be illustrative and not limiting.

EXAMPLE 1

5 Variations in the gelation time of hydroxypropyl guar (HPG) solutions using different sources of borate ion are measured below.

HPG (2.5 gm or 0.5 wt.%) was dissolved in 500 ml of tap water at room temperature (approximately 75°F) and NaOH was added to adjust the pH of the HPG solution to a pH of approximately 11 to 12 (i.e., 0.025 wt.%).

10 A Waring blender set on low speed served to mix the HPG solution. The HPG solution (500 ml) was poured into the Waring blender cup, which had a total cup capacity of approximately 1 liter. The blender was connected to a rheostat and the rheostat adjusted to 45% of the full scale. When the HPG solution was stirred in this manner a vortex was produced in the HPG solution that extended almost to the blender blades. Mixing the HPG solution as described provided a moderate
15 mixing of the HPG solution that simulated the mixing observed in field tanks. The borate source was added to the vortexing solution and the gelation time measured. The gelation time is the time interval from the addition of the borate until a substantially non-flowing gel is produced. In addition to the gelation time, the time interval from the addition of the borate until the vortex began to close, indicating that gelation has begun, was also recorded.

20 When 0.3 gm (0.06 wt.%) of Borax was added to the vortexing HPG solution, gelation occurred at room temperature in less than 30 seconds. In contrast, when 1.5 gm (0.3 wt.%) of 20/40 mesh ulexite was added to an HPG solution of the same concentration, the vortex began closing in approximately 20 minutes at room temperature. Gelation of the HPG solution was almost complete in 27 minutes and was totally complete within 80 minutes, providing
25 approximately a 30 minute delay in the gelation of the HPG solution. About an hour delay in the gelation reaction was achieved when 1.5 gm (0.3 wt.%) of anhydrous sodium tetraborate particles approximately 12 mesh in size were added to the HPG solution. The addition of the anhydrous sodium tetraborate to the HPG solution began to close the vortex in 45 minutes and gelation of the HPG solution was almost complete in 65 minutes.

EXAMPLE 2

30 The temperature dependence of the borate crosslinking of HPG solutions is illustrated below.

HPG (2.5 gm or 0.5 wt.%) was dissolved in 500 ml of tap water and NaOH was added to

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adjust the pH of the HPG solution to a pH of approximately 11 to 12 (i.e., 0.025 wt.%).

A Waring blender set on low speed served to mix the HPG solution. The HPG solution (500 ml) was poured into the Waring blender cup, which had a total cup capacity of approximately 1 liter. The blender was connected to a rheostat and the rheostat adjusted to 45% of the full scale.

5 When the HPG solution was stirred in this manner a vortex was produced in the HPG solution that extended almost to the blender blades. Mixing the HPG solution as described provided a moderate mixing of the HPG solution that simulated the mixing observed in field tanks. The borate source was added to the vortexing solution and the gelation time measured. The gelation time is the time interval from the addition of the borate until a substantially non-flowing gel is produced. In
10 addition to the gelation time, the time interval from the addition of the borate until the vortex began to close, indicating that gelation had begun, was also recorded.

When 0.5 gm (0.1 wt.%) of 20/40 mesh ulexite was added to the HPG solution at 120°F the vortex closed in approximately 6 minutes. Gelation of the HPG solution was almost complete in 10 minutes and was totally complete within 12 minutes. The final temperature of the HPG
15 solution was 102°F. The same procedure was repeated with the HPG solution at 126°F, although during the course of the experiment the temperature decreased to 105°F. Once the ulexite was added, the vortex closed in 9 minutes and gelation was complete within 17 minutes.

In contrast, when 0.5 gm (0.1 wt.%) of 20/40 mesh ulexite was added to the HPG solution at 68°F no crosslinking of the HPG solution was observed for 40 minutes. The HPG solution was
20 heated to 72°F and observed for another 10 minutes. No crosslinking was seen. The HPG solution was then heated to 115°F and the HPG solution crosslinked within 5 minutes.

Gelation of the HPG solution occurred within 1 minute when 1.0 gm (0.2 wt.%) of anhydrous sodium tetraborate (particles smaller than 12 mesh) was added to the HPG solution at 128°F. However, the addition of the same quantity of anhydrous sodium tetraborate to the HPG
25 solution at 70°F did not cause gelation of the HPG solution within 50 minutes of the addition of borate. The addition of the anhydrous sodium tetraborate caused the vortex to close at 38 minutes, but the solution remained viscous and did not crosslink throughout the 50 minute observation period.

30 EXAMPLE 3

Variations in the gelation time of hydroxypropyl guar (HPG) solutions using different concentrations of anhydrous sodium tetraborate at different temperatures was measured as described below.

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HPG (2.5 gm or 0.5 wt.%) was dissolved in 500 ml of tap water and NaOH was added to adjust the pH of the HPG solution to a pH of approximately 11 to 12 (i.e., 0.025 wt.%).

A Waring blender set on low speed served to mix the HPG solution. The HPG solution (500 ml) was poured into the Waring blender cup, which had a total cup capacity of approximately 1 liter. The blender was connected to a rheostat and the rheostat adjusted to 45% of the full scale. When the HPG solution was stirred in this manner a vortex was produced in the HPG solution that extended almost to the blender blades. Mixing the HPG solution as described provided a moderate mixing of the HPG solution that simulated the mixing observed in field tanks. Anhydrous sodium tetraborate (particles smaller than 12 mesh) was added to the vortexing solution at three different concentrations at various temperatures. The gelation time was measured and recorded. The gelation time is the time interval from the addition of the anhydrous sodium tetraborate until a substantially non-flowing gel is produced. In addition to the gelation time, the time interval from the addition of the borate until the vortex began to close, indicating that gelation has begun, was also recorded.

When 0.75 gm (0.15 wt.%) anhydrous sodium tetraborate (particles smaller than 12 mesh) was added to the HPG solution at 108°F crosslinking of the HPG solution occurred between 14 and 16 minutes. When the same concentration of anhydrous sodium tetraborate was added to the HPG solution at 98°F the vortex began to close in 10 minutes and crosslinking continued throughout the next 5 minutes, but the HPG solution was never completely crosslinked within the 15 minute observation period.

When 0.4 gm (0.08 wt.%) of anhydrous sodium tetraborate was added to the HPG solution at 100°F the vortex began to close in 23 minutes. The vortex had not completely closed at 32 minutes. The solution was then heated to 136°F and crosslinking occurred in 7 minutes.

When 0.25 gm (0.25 wt.%) of anhydrous sodium tetraborate was added to the HPG solution at 105°F no crosslinking was observed for 13 minutes. During the course of the experiment, the temperature decreased to 96°F and the vortex began to close over the next 7 minutes. After 45 minutes, crosslinking was still incomplete. The solution was then heated to 120°F and the solution crosslinked rapidly. Similarly, when the same concentration of anhydrous sodium tetraborate was added to the HPG solution at 102°F no crosslinking was observed for 14 minutes. The solution cooled to 100°F and the vortex began to close within the next 6 minutes, yet even after a total of 37 minutes the solution had not completely crosslinked. The heated sample crosslinked rapidly; however, the non-heated HPG solution did not crosslink in that same time period.

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The foregoing examples, exemplify that a galactomannan solution at pH 11 can be mixed with a slowly soluble borate source in a stirred tank at or near 100°F for several minutes without crosslinking. Then when the polysaccharide solution is pumped down the well bore and heats to the reservoir temperature the solution will crosslink and serve to prevent lost circulation.

5 Convenient and economical preparations and low pumping friction pressures can thus be achieved by the delaying the crosslinking of the guar solutions on the surface and in the pipeline, while providing sufficient concentrations of borate at higher temperatures to ensure the gelation of the LCM fluid in the well bore.

10 The times and the temperatures observed in the examples above are useful for field applications. The gelation of the polysaccharide solutions can be controlled by temperature or concentration of the borate source. The proper concentration of the slowly soluble borate source ensures that the LCM fluid crosslinks in the well bore and not in the storage tank, the mixing tank or in the pipeline to the well bore.

15 The rate of dissolution and borate ion release by the borate solids depends strongly on particle size distributions. Appropriate borate sources are available as dry solids. These can be suitably sized prior to application. But grinding and size changes are apt to occur during transportation to the rig site and subsequent inadvertent abuse during handling. Size stability and ease of mixing can be improved by transporting and applying the water soluble borates in an oil carrier fluid. However, oils used in offshore drilling must meet stringent environmental standards.

20 A suitable oil is an environmentally friendly ester such as described in U.S. Patent No. 5,252,554. Other environmentally friendly oils can also be used. Borate solids can be kept suspended in the oil carrier by a suitable suspending agent such as an organophilic clay.

2. Zirconate Crosslinking Agents

25 Organic esters of zirconium were also tested as delayed crosslinkers for guar polymer carriers of LCMs. Organic zirconium complexes have been described as crosslinking agents for crosslinkable polysaccharides in U.S. Patent Nos. 4,460,751, 4,657,081, 4,749,041 and 4,797,216. The description of these zirconium complexes in the aforementioned patents is hereby incorporated by reference.

30 Table 1 contains a summary of test results using an organic ester of zirconium as a crosslinker for carboxymethyl hydroxypropyl guar (CMHPG). The organic ester of zirconium used to obtain the test results of Table 1 is commercially available from Halliburton Energy Services, Inc., Houston, Texas under the brand name CL-24™. All of the samples given in Table 1 were prepared in 3% KCl.

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The method of testing was to circulate, using a positive displacement pump, test solutions through a coil of 3/8 inch diameter tubing, approximately 6 feet long and immersed in a temperature bath. The samples were initially circulated at a low temperature (90°F or less) to simulate mixing on a rig floor. The temperature was increased as the samples continued to circulate and the time required for the samples to gel at the increased temperature was observed.

Data in Table 1 show that guar polymer solutions (0.6 wt.% to 0.82 wt.%) containing zirconium ester (0.05 vol% to 0.068 vol%) can be mixed for at least 20 minutes at temperatures of 90°F or less without crosslinking. Solutions having a pH greater than pH 10 crosslinked in about 10 minutes or less once the temperature of the solutions were raised to 120°F or greater. Sample 9 having a pH of 8 did not crosslink in more than 30 minutes at 120°F.

Thus guar polymer solutions and zirconium crosslinkers can be mixed on the surface at the rig floor with no danger of crosslinking provided the fluid temperature is at or below about 110 ° F. The crosslinking of the guar solutions can be controlled with temperature or pH. If the pH of a guar solution is over about pH 10, then the solution will crosslink once it is injected into lost circulation zones or fractures and is heated to reservoir temperatures.

Table 1
Delayed Crosslink Tests With an Organic Zirconate

Sample	Guar Conc. (wt.%)	pH	Sodium Carbonate (ppt)	Cross-linker (vol.%)	Initial Viscosity (cP)	Lower Temp (°F)	Circulating Time (min)	Viscosity After Circulating (cP)	Elevated Temp (°F)	Circulating Time (min)	Final Viscosity
1	0.72	11	10	0.06	58	90	20	76	120	4.6	SC
2	0.72	10	10	0.06	56	90	20	61	130	10.6	SC
3	0.82	11	10	0.068	68	90	20	93			
4	0.82	11	10	0.068	68	room	>30	No Change	124	2.5	SC
5	0.82	10	10	0.068	68	room	>31	No Change	120	8	SG
6	0.6	11	10	0.05	50	room	>32	No Change	82	>30	61cP
7	0.6	11	10	0.05	50	room	>33	No Change	120	3.4	SC
8	0.6	10	10	0.05	50	room	>34	No Change	120	6.2	SC
9	0.6	8	10	0.05	50	room	>35	No Change	120	>30	53.5cP

cP = centipoise
ppt = pounds per thousand gallons of LCM fluid
SC = strong crosslink

3. Titanate Crosslinking Agents

Organic esters of titanium were also tested as delayed crosslinkers for guar polymer carriers of LCMs. U.S. Patent Nos. 4,470,915, 4,462,917, 4,464,270 and 4,502,967 describe the use of an organotitanate chelate as a crosslinking agent in fracturing fluids. The description of these titanate compounds in the aforementioned patents is hereby incorporated by reference.

Table 2 contains a summary of test results using an organic ester of titanium as a crosslinker for underivatized guar. The organic ester of titanium used to obtain the test results of Table 2 is commercially available from Halliburton Energy Services, Inc., Houston, Texas under the brand name CL-18™. All of the samples given in Table 2 contained 25 pounds per barrel of finely divided cellulose to serve as a fluid loss material.

The method of testing was to circulate, using a positive displacement pump, test solutions through a coil of 3/8 inch diameter tubing, approximately 6 feet long and immersed in a temperature bath. The samples were initially circulated at a low temperature (90°F or less) to simulate mixing on a rig floor. After 20 minutes, the temperature was increased as the samples continued to circulate and the time required for the samples to crosslink at the increased temperature was observed.

Data in Table 2 show that guar polymer solutions (0.6 wt% to 0.72 wt.%) containing titanium organic ester (0.3 vol% to 0.5 vol%) can be mixed for at least 20 minutes at temperatures of 90°F or less without crosslinking. The present invention uses a combination of crosslinker concentration and pH that will ensure crosslinking of the LCM fluid at temperatures of 120° F. or higher.

Thus selected concentrations of guar polymer solutions and titanium crosslinkers can be mixed on the surface at the rig floor with no danger of crosslinking. The crosslinking of the guar solutions is controlled with temperature and pH. If the pH of a guar solution containing about 0.4 vol% of crosslinker is over about 10, then the solution will crosslink when it is injected into lost circulation zones or fractures and is heated to reservoir temperatures.

Table 2
Delayed Crosslink Tests With an Organic Titanate

Sample	Water Type	Guar (wt.%)	Cross-linker (vol.%)	pH	Barite (ppb)	Fluid Density (ppg)	Lower Temp (°F)	Initial Viscosity (cP)	Circulating Time (min)	Final Viscosity (cP)	Elevated Temp (°F)	Circulating Time (min)	Final Viscosity
1	3 wt.% KCl	0.6	0.3	9	0	8.7	80	78	20	76	122	17	S.C.
2	10 ppg NaCl	0.6	0.3	10	0	10.1	80	88	20	84	120	40	96cP
3	10 ppg NaCl	0.6	0.4	8.6	0	10.1	87	108	20	112	123	45	M.C.
4	10 ppg NaCl	0.6	0.5	8.5	0	10.1	78	98	20	105	119	55	M.C.
5	10 ppg NaCl	0.72	0.35	10	0	10.1	83	110	20	88	127	18	S.C.
6	10 ppg NaCl	0.72	0.35	10	150	11.7	81	165	20	87	146	25	S.C.
7	3 wt.% KCl	0.6	0.3	9.9	150	11.2	76	101	20	83	93	40	100cP
8	3 wt.% KCl	0.72	0.35	9.9	160	11.3	78	134	20	128	120	55	142cP
9	3 wt.% KCl	0.72	0.4	9.9	160	11.3	82	128	20	127	120	30	S.C.

ppg = pounds per gallon
ppb = pounds per barrel
10 ppg NaCl = an NaCl solution of density equal to 10 ppg
S.C. = Strong Crosslink
M.C. = Moderate Crosslink

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Thus compositions and methods for the gelation of LCM fluids containing cross-linkable polysaccharides such as galactomannan have been described that provide the mixing of the LCM fluid components in the mixing tank at the surface without having to specify or tightly control the holding and pumping times of the solution. The flexibility of the described system provides a simple and inexpensive process for preparing and using LCM fluids to prevent extensive mud loss.

The LCM fluids are used to suspend solids that can be circulated to highly permeable regions or fractures to bridge and seal the permeable formations and prevent the fractures from growing. Examples of suitable insoluble solids or particulates are calcium carbonate, acid soluble mineral fibers, cellulose fibers, deformable graphite particles, and nut shells.

Additional optional components of the LCM fluids include weighting material such as barite. Environmentally friendly esters, such as a monocarboxylic acid ester of a C₂ to C₁₂ monofunctional alkanol (an example of which is PETROFREE™ available from Baroid Drilling Fluids, Houston, Texas) can also be used to suspend the solid crosslinkers so that they can be added as a liquid to the LCM fluid.

Another advantage of the described system is that the galactomannan gels can be broken by formation fluids, and by acids or oxidizers to form non-damaging residues.

Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the invention as defined by the appended claims.

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We claim:

1. A process for preparing a fluid used to suspend lost circulation material solids comprising:
 - (a) obtaining a surface tank at a temperature of 110°F or less;
 - (b) preparing the fluid in the surface tank, wherein the preparation of the fluid includes mixing a water-soluble crosslinkable polysaccharide in an amount sufficient to gel the fluid, a crosslinking agent present at a concentration sufficient to crosslink at least a portion of the polysaccharide, and a quantity of lost circulation material solids;
 - (c) pumping the fluid into the well bore; and
 - (d) crosslinking the polysaccharide to produce a crosslinked gel within the well bore at a temperature greater than 110°F.
2. The process of claim 1, wherein the water-soluble crosslinkable polysaccharide is a galactomannan.
3. The process of claim 1, wherein the water-soluble crosslinkable polysaccharide is a guar or guar derivative.
4. The process of claim 1, wherein the crosslinking agent is a slowly soluble, or otherwise slowly released, source of borate.
5. The process of claim 4, wherein the borate is an anhydrous sodium tetraborate or ulexite.
6. The process of claim 1, wherein the crosslinking agent is an organic ester of titanium or zirconium.
7. The process of claim 1, wherein the polymer will not crosslink for a time sufficient to allow batch mixing at temperatures of 90° F or less.

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- 1 8. A drilling fluid comprising:
2 a quantity of lost circulation material solids;
3 a crosslinkable galactomannan at a concentration ranging from about 0.2 to 1.5 percent of the
4 weight of the fluid;
5 a base or buffer;
6 a crosslinking agent at a concentration ranging from 0.5 to 1.0 percent of the volume of the
7 fluid;
8 wherein the pH of the fluid and the concentration of the components of the fluid are selected
9 such that the polysaccharide will crosslink within 1 hour at a temperature of 120°F or greater.
- 1 9. The fluid of claim 8, further comprising weighting material.
- 1 10. The fluid of claim 8, further comprising a gel breaker.
- 1 11. The fluid of claim 8 wherein the water soluble crosslinkable polysaccharide is a guar or guar
2 derivative.
- 1 12. The fluid of claim 8, wherein the crosslinking agent is a slowly soluble source of borate.
- 1 13. The fluid of claim 8, wherein the metallic crosslinker is an organic ester of titanium or
2 zirconium.