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(72) Inventeurs/Inventors:
DOBSON, JAMES W., JR., US;
TRESCO, KIM O., US

(73) Propriétaire/Owner:
TEXAS UNITED CHEMICAL COMPANY, LLC, US

(74) Agent: KIRBY EADES GALE BAKER

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(54) Title: METHOD OF DELAYING THE SETTING TIME OF CROSSLINKED LOST CIRCULATION CONTROL PILLS

(57) Abrégé/Abstract:
There is disclosed a method of delaying the setting time of aqueous lost circulation control pills. The aqueous lost circulation control pills contain a crosslinkable polymer viscosifier, one or more water retention additives, a crosslinking agent, a pH control agent, and a crosslink time regulator. The method comprises utilizing as the crosslink time regulator encapsulated sodium chloride. The preferred crosslinkable polymer is xanthan gum. The preferred water retention additives are pregelatinized starch and a polyanionic cellulose derivative. The preferred crosslinking agent is a hydrated borate. The preferred pH control agent is magnesium oxide. Preferably the sodium chloride is encapsulated with a urethane coating.

ABSTRACT

There is disclosed a method of delaying the setting time of aqueous lost circulation control pills. The aqueous lost circulation control pills contain a crosslinkable polymer viscosifier, one or more water retention additives, a crosslinking agent, a pH control agent, and a crosslink time regulator. The method comprises utilizing as the crosslink time regulator encapsulated sodium chloride. The preferred crosslinkable polymer is xanthan gum. The preferred water retention additives are pregelatinized starch and a polyanionic cellulose derivative. The preferred crosslinking agent is a hydrated borate. The preferred pH control agent is magnesium oxide. Preferably the sodium chloride is encapsulated with a urethane coating.

METHOD OF DELAYING THE SETTING TIME OF CROSSLINKED LOST CIRCULATION CONTROL PILLS

Background of the Invention

The invention provides a means of delaying the setting time of lost circulation control pills containing one or more polymeric materials and a crosslinking agent/additive which reacts with and crosslinks the polymeric materials.

It is well known in the oil and gas drilling and servicing art to pump a lost circulation control pill in a wellbore to stop and prevent the loss of the drilling or servicing fluid to the surrounding subterranean formations being drilled.

Crosslinkable polymer-containing lost circulation control pills (hereinafter sometimes referred to as "CPCLCCP") are well known in the art. See for example: FLEX-PLUG™, a product of Halliburton Energy Services, Inc.; POLY-PLUG®; a product of M&D Industries; X-LINK®, a product of Baker Hughes Inteq; FORM-A-SET™, a product of M-I SWACO; PBS PLUG SYSTEM™, a product of Texas United Chemical Company, LLC. (dba TBC-BRINADD); and VEN-PLUG™, a product of Venture Chemicals, Inc. Such CPCLCCP contain one or more crosslinkable polymers and a crosslinking agent therefore. Properly formulated, the crosslinking of the crosslinkable polymer results in a CPCLCCP which increases in viscosity until the pill is "set" into a firm mass which may be pliable or semi-solid to solid. The set pills are generally referred to as "plugs" in the art as they plug the

crevices, fractures, and other open spaces within the formation where lost circulation is occurring.

Crosslinkable polymer-containing fluids have been used in the oil and gas well drilling and servicing industry for many uses, particularly as formation fracturing fluids. In order to control the crosslinking time (time to complete the crosslinking of the polymer with the crosslinking agent), or the breaking time (time to decrease the viscosity of the fluid after it has performed its function) of the fluid, various components of the fluids have been encapsulated with a coating which temporarily decreases the solubility and/or reactivity of the components. See for example the following list of U.S. Patents in which the components encapsulated are given in parenthesis: 4,036,301 (cement accelerator); 4,362,566 (reaction initiator or accelerator); 4,664,816 (water absorbent polymer); 4,704,213 (oil absorbent polymer); 4,741,401 (breaker); 5,373,910 (breaker); 5,981,447 (breaker); 6,209,646 (liquid chemical additive); 6,387,986 (crosslinking agent); 6,422,314 (oxidizer or other breakers); 6,444,316 (water soluble chemicals); 6,494,263 (oxidizer or other breakers); 6,527,051 and 6,554,017 (water soluble chemicals including solid acid forming materials); 6,569,814 (ammonium persulfate oxidizer breaker); 6,642,185 (divalent cation releasing materials, i.e., calcium chloride); 6,667,279 (swelling agent); 6,702,044 (acid catalyst); 6,767,868 (breaker).

Summary of the Invention

The present invention provides an improved crosslinkable polymer-containing lost circulation control pill and a method of delaying the time to crosslink or "set" the pill. A CPCLCCP is formulated to be fluid and pumpable when initially prepared. It is

then pumped down a borehole to the formation where lost circulation is occurring. Ideally the crosslinking reaction of the polymer is controlled such that the pill increases in viscosity and becomes a semi-solid or gelled fluid upon entering the subterranean formation. Thereafter the crosslinking continues and a solid mass is obtained which fills the formation's cavities, pores, fractures, and the like thus preventing further loss of the borehole fluid to the formation.

The CPCLCCP comprises an aqueous liquid, a crosslinkable polymer visocosifier, one or more water retention additives, a crosslinking agent, a pH control agent, and an encapsulated sodium chloride crosslink time regulator.

The method of delaying the crosslink time of the CPCLCCP comprises adding to the CPCLCCP sodium chloride which has been encapsulated to provide a coating which regulates the solublization time of the sodium chloride in the aqueous phase of the CPCLCCP.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof will hereinafter be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the invention is to cover all modifications and alternatives falling within the scope of the invention as expressed in the appended claims.

The compositions can comprise, consist essentially of, or consist of the stated materials. The method can comprise, consist essentially of, or consist of the stated steps with the stated materials.

Detailed Description of the Invention

In a particular embodiment the invention is directed to a method of delaying the setting time of aqueous crosslinked lost circulation control pills, the method which comprises:

a) providing an aqueous fluid comprising:

i. water;

ii. a crosslinkable polymer viscosifier;

iii. one or more water retention additives; and

iv. a crosslinking agent; and

b) adding to the aqueous fluid a pH control agent and an encapsulated sodium chloride crosslink setting time regulator comprising particulate sodium chloride,

wherein the setting time of the lost circulation control pills is delay by the regulated release and solubilization of sodium chloride into the aqueous phase of the fluid.

The CPCLCCP of the invention comprises:

(a) a crosslinkable polymer viscosifier;

(b) one or more water retention additives;

(c) a crosslinking agent;

(d) a pH control agent; and

(e) an encapsulated sodium chloride crosslink time regulator.

The crosslinkable polymer viscosifier in the CPCLCCP of the invention may be selected from any such polymers well known in the art. Representative polymers include various hydratable polysaccharides or polysaccharide derivatives such as guar gum, hydroxyalkylguar, hydroxyalkylcellulose, carboxyalkylhydroxyalkylguar, carboxyalkylhydroxyalkylcellulose, various other cellulose ethers, biopolymers, scleroglucan, succinoglucan, and the like.

The biopolymer viscosifier useful in the practice of this invention is preferably a xanthomonas gum (xanthan gum). Xanthomonas gum is available commercially. It is a widely used viscosifier and suspending agent in a variety of fluids, Xanthomonas gum can be made by the fermentation of carbohydrate with bacteria of the genus Xanthomonas. Representative of these bacteria are Xanthomonas campestris, Xanthomonas phaseoli, Xanthomonas mulvacearn, Xanthomonas carotoe, Xanthomonas traslucens, Xanthomonas hederae, and Xanthomonas papavericoli. The gum produced by the bacteria Xanthomonas campestris is preferred for the purpose of this invention. The fermentation usually involves inoculating a fermentable broth containing a carbohydrate, various minerals and a nitrogen yielding compound. A

number of modifications in the fermentation procedure and subsequent processing are commercially used. Due to the variety of fermentation techniques and difference in processing operation subsequent to fermentation, different production lots of xanthomonas gum will have somewhat different solubility and viscosity properties. Xanthomonas gums useful in the practice of the present invention are relatively hydratable xanthomonas gums.

The colloid is a polymer containing mannose, glucose, glucuronic acid salts such as potassium glucuronate, sodium glucuronate, or the like, and acetyl radicals. Other Xanthomonas bacteria have been found which produce the hydrophilic gum and any of the xanthan gums and their derivatives can be used in this invention. Xanthan gum is a high molecular weight linear polysaccharide that is readily soluble in water to form a viscous fluid.

Other biopolymers prepared by the action of other bacteria, or fungi, on appropriate fermentation mediums may be used in the fluids of the present invention provided that they impart the desired synergistic thermally stable rheological characteristics thereto. This can be readily determined by one skilled in the art in accordance with the teachings of this specification.

The term "biopolymer" is intended to mean an excellular polysaccharide of high molecular weight, in excess of 200,000, produced by fermentation of a carbohydrate source by the action of bacteria or fungi. Representative microorganisms are the genus Xanthomonas, Pseudomonas, Agrobacterium, Arthrobacter, Rhizobium, Alcaligenes, Beijerincka, and Sclerotium. A succinoglucan type polysaccharide

produced by microorganisms such as NCIB 11592 and NCIB 11883 is commercially available.

Xanthan gum is preferred.

The water retention additive is present in the CPCLCCP to prevent the pill from losing water and thus "drying out" before the crosslinkable polymer viscosifier has been fully crosslinked. Such "drying out" of the pill produces a non-cohesive, crumbly pill. Representative water retention additives are starch, starch derivatives, cellulose derivatives, hydrophilic polymers, and the like, such as hydroxyalkylstarch, carboxymethylstarch, hydroxyalkylcarboxymethylstarch, hydroxyalkylcellulose, carboxymethylcellulose, hydroxyethylcarboxymethylcellulose, other polysaccharides, polyvinyl alcohol, partially hydrolyzed polyacrylamides, and mixtures thereof.

Various crosslinkable polymer viscosifiers and polysaccharides and derivatives thereof which may be used as water retention additives are set forth in Dobson, Jr. et al. U.S. Patent No. 6,800,593.

The crosslinking agent of the invention is dependent upon the crosslinkable polymer viscosifier used in formulating the CPCLCCP as is well known in the art. The preferred crosslinking agents are hydrated borates of alkali metals and/or alkaline earth metals, such as sodium borates, calcium borates, and sodium calcium borates. Ulexite, $NaCaB_5O_9 \cdot 8H_2O$, and probertite, $NaCaB_5O_9 \cdot 5H_2O$, are representative hydrated alkali metal alkaline earth metal borates. Colemenite, $Ca_2B_6O_{11} \cdot 5H_2O$, is a representative alkaline earth metal borate. See for example Mondshine U.S. patent No. 4,619,776.

The pH control agent of the invention is preferably magnesium oxide.

The pH of the CPCLCCP must be at least 8 in order for the borate crosslinking of the crosslinkable polymer viscosifier to occur, preferably from about 8 to about 13, most preferably from about 9 to about 12.

The encapsulated sodium chloride crosslink time regulator (hereinafter sometimes referred to as "ESCCTR") of the invention is particulate sodium chloride which has been encapsulated with one or more coatings to decrease the rate of solublization of the sodium chloride.

Known methods and materials for encapsulating particulate water soluble materials can be used to encapsulate the particulate sodium chloride. See for example the following U.S. Patents: Walles et al. 4,741,401; Normal et al. 5,373,901; Markusch et al. 6,165,550; Moradi-Araghi et al. 6,387,986; and Reddy et al. 6,444,316.

In order to more completely describe the invention, the following non-limiting examples are given. In these examples and this specification, the following abbreviations may be used: bbl = 42 gallon barrel; ppb = pounds per 42 gallon barrel; °F = degrees Fahrenheit; g = grams; mm = millimeter; hr = hours. All percentages are present by weight of the coated particulate sodium chloride (sodium chloride plus coating).

Example 1

Lost circulation control pills were prepared containing 290.5 g (0.83 bbl equivalent) of fresh water, 100 g (ppb) of PBS PLUG® 500, a mixture of xanthan biopolymer, pregelatinized corn starch, polyanionic cellulose, and sized borate salts available from TBC-Brinadd, Houston, Texas U.S.A., and 50 g (ppb) of PBS PLUG

activator, a mixture of magnesium oxide and sodium chloride also available from TBC-Brinadd, Houston, Texas U.S.A.

The particulate sodium chloride in the PBS PLUG activator was coated with 0%, 12%, 16%, 20% or 24% by weight of a urethane coating by Fritz Industries, Inc.

The pills were dynamically aged at 150°F by placing the pills in jars and hot rolling. The pills were visually observed after 1, 2, and 3 hours aging. The results observed are set forth in Table 1.

The results indicate that the encapsulation of the sodium chloride with the urethane increased the setting time of the pills. The setting time increased as the concentration of the urethane coating increased.

Table 1

Visual Observations

Dynamically Aged @ 150°F, 3 hours

	0%	12%	16%	20%	24%
Initial	Fluid	Fluid	Fluid	Fluid	Fluid
1 hr	Set	Slow Pour	Slow Pour	Slow Pour	Slow Pour
2 hr	Set	Slow Pour	Slow Pour	Slow Pour	Slow Pour
3 hr	Set	½ Set	½ Set	¼ Set	Slow Pour

Example 2

Lost circulation control pills were prepared as in Example 1. The pills were static aged at 150°F for 19 hours, cooled to room temperature, and the hardness of the pills measured with a penetrometer. The data are set forth in Table 2.

Example 3

Two lost circulation pills were prepared as in Example 1 with the particulate sodium chloride containing a coating of 24% by weight urethane. One pill was dynamically aged at 150°F and visually observed after 1, 3, and 5 hours aging. The pill remained fluid throughout the testing. The other pill was static aged at 150°F and the hardness of the pill was determined after 16 hours and 80 hours aging. The penetrometer readings were 32 mm and 23 mm, respectively.

Table 2

Penetrometer Readings, mm

Stated Aged @ 150°F, 19 hours

0%	12%	16%	20%	24%
7	9	10	15	17

Claims:

1. A method of delaying the setting time of aqueous crosslinked lost circulation control pills, the method which comprises:

a) providing an aqueous fluid comprising:

i. water;

ii. a crosslinkable polymer viscosifier;

iii. one or more water retention additives; and

iv. a crosslinking agent; and

b) adding to the aqueous fluid a pH control agent and an encapsulated sodium chloride crosslink setting time regulator comprising particulate sodium chloride,

wherein the setting time of the lost circulation control pills is delay by the regulated release and solubilization of sodium chloride into the aqueous phase of the fluid.

2. The method of claim 1 wherein the crosslinkable polymer viscosifier is xanthan gum.

3. The method of claim 1 wherein the crosslinkable polymer viscosifier is selected from the group consisting of guar gum, hydroxyalkylguar, carboxyalkylhydroxyalkylguar, hydroxyalkylcellulose, carboxyalkylhydroxyalkylcellulose, biopolymers, and mixtures thereof.

4. The method of claim 3 wherein the one or more water retention additives are selected from the group consisting of starch, starch derivatives, cellulose derivatives, hydrophilic polymers, and mixtures thereof.

5. The method of claim 4 wherein the one or more water retention additives are selected from the group consisting of starch, hydroxyalkylstarch, carboxymethyl starch, carboxymethylhydroxyethylstarch, hydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethylcellulose, polyvinyl alcohol, partially hydrolyzed polyacrylamides, and mixtures thereof.

6. The method of claim 1 wherein the crosslinking agent is a hydrated borate selected from the group consisting of sodium borates, calcium borates, sodium calcium borates, and mixtures thereof.

7. The method of claim 1 wherein the pH control agent is magnesium oxide.

8. The method of claim 1, 2, 3, 4, 5, 6, or 7 wherein the sodium chloride is encapsulated with a urethane coating.

9. The method of claim 3, 4, 5, 6, or 7 wherein the crosslinkable polymer is xanthan gum.

10. The method of claim 9 wherein the sodium chloride is encapsulated with a urethane coating.