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(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **YOU, Fengxiang** [CN/US]; 1076 Ryans Run, Garnet Valley, PA 19061 (US).

(74) Agent: **SANCHEZ, Kathryn, M.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

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(54) Title: HIGH TEMPERATURE AQUEOUS-BASED ZIRCONIUM FRACTURING FLUID AND USE

(57) Abstract: A fracturing fluid or crosslinking composition suitable for use at high temperature (275-340°F, 135-171°C) comprising (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to provide a pH less than 9, (e) an organic acid, (f) hydroxypropyl guar and (g) a zirconium crosslinking agent. The composition is useful as a fracturing fluid in oil field applications, for example, for hydraulically fracturing a subterranean formation or selectively plugging a permeable zone or leak in a subterranean formation.



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TITLE**HIGH TEMPERATURE AQUEOUS-BASED  
ZIRCONIUM FRACTURING FLUID AND USE**FIELD OF THE INVENTION

5           The present invention relates to zirconium-based crosslinking compositions and their use in oil field applications such as hydraulic fracturing and plugging of permeable zones.

BACKGROUND OF THE INVENTION

          The production of oil and natural gas from an underground well  
10   (subterranean formation) can be stimulated by a technique called hydraulic fracturing, in which a viscous fluid composition (fracturing fluid) containing a suspended proppant (e.g., sand, bauxite) is introduced into an oil or gas well via a conduit, such as tubing or casing, at a flow rate and a pressure which create, reopen and/or extend a fracture into the oil- or  
15   gas-containing formation. The proppant is carried into the fracture by the fluid composition and prevents closure of the formation after pressure is released. Leak-off of the fluid composition into the formation is limited by the fluid viscosity of the composition. Fluid viscosity also permits suspension of the proppant in the composition during the fracturing  
20   operation. Cross-linking agents, such as borates, titanates or zirconates, are usually incorporated into the fluid composition to control viscosity.

          Typically, less than one third of available oil is extracted from a well after it has been fractured before production rates decrease to a point at which recovery becomes uneconomical. Enhanced recovery of oil from  
25   such subterranean formations frequently involves attempting to displace the remaining crude oil with a driving fluid, e.g., gas, water, brine, steam, polymer solution, foam, or micellar solution. Ideally, such techniques (commonly called flooding techniques) provide a bank of oil of substantial depth being driven into a producing well; however, in practice this is  
30   frequently not the case. Oil-bearing strata are usually heterogeneous, some parts of them being more permeable than others. As a

consequence, channeling frequently occurs, so that the driving fluid flows preferentially through permeable zones depleted of oil (so-called "thief zones") rather than through those parts of the strata which contain sufficient oil to make oil-recovery operations profitable.

5           Difficulties in oil recovery due to thief zones may be corrected by injecting an aqueous solution of an organic polymer and a cross-linking agent into a subterranean formation under conditions where the polymer will be cross-linked to produce a gel, thus reducing permeability of the subterranean formation to driving fluid (gas, water, etc.). Polysaccharide-  
10 or partially hydrolyzed polyacrylamide-based fluids cross-linked with certain aluminum, titanium, zirconium, and boron based compounds are used in these enhanced oil recovery applications.

Cross-linked fluids or gels, whether for fracturing a subterranean formation or for reducing permeability of zones in subterranean formation,  
15 are now being used in hotter and deeper wells under a variety of temperature and pH conditions, where rates of cross-linking with known cross-linking compositions may be unacceptable.

Commercially available zirconium complexes of triethanolamine do not cross-link at desirable rates for all organic polymers, for example, too  
20 fast, or they do not maintain adequate viscosity in the cross-linked fluid under high pH conditions and/or temperatures of about 275°F (135°C) and higher, causing a significant loss in viscosity due to shear degradation, which can also result in a sand out. Sand out refers to a situation in which sand (proppant) deposits at the bottom of a wellbore due to lack of  
25 viscosity development of the cross-linked fluid before the fluid reaches the fracture zone.

U.S. Patent 4,801,389 discloses a fracturing fluid consisting of a natural guar gum useful at high temperature (250 to 325°F, 121 to 163°C). The fluid pH is controlled using a bicarbonate salt at a pH of 8 to 10 and  
30 further comprises a zirconium crosslinking agent such as zirconium lactate, sodium thiosulfate, brine (KCl). Use of bicarbonate shows

acceptable viscosity (113 cp at  $170 \text{ sec}^{-1}$  at 1 hour,  $121^\circ\text{C}$ ,  $250^\circ\text{F}$ ). In contrast, use of sodium carbonate shows poor viscosity (23 cp) under the same conditions.

U.S. Patent 6,737,386 discloses a fracturing fluid comprising  
5 natural guar and temperatures of  $250$  to  $340^\circ\text{F}$  ( $121$  to  $171^\circ\text{C}$ ). The fluid has a pH range of 9 to 12 and comprises zirconium crosslinker, brine, sodium thiosulfate, a buffer and citric acid. The fracturing fluids provide a 4-hour viscosity between 200-300 cp at  $340^\circ\text{F}$  at a shear rate of  $40 \text{ sec}^{-1}$  using natural guar.

10 There is a need for fracturing fluids which can function at high temperatures ( $\geq 275^\circ\text{F}$ ,  $135^\circ\text{C}$ ) and provide sufficient viscosity at these temperatures when using hydroxypropyl guar. HPG is a solvatable polysaccharide that is commercially available. Compared to natural guar, HPG is more soluble in water, which may minimize damage to a  
15 subterranean formation. HPG also has a faster hydration rate, which may minimize agglomerate formation when dissolving in water. However, when HPG is crosslinked using a zirconium crosslinker under certain conditions, such as at high temperature, viscosity is unacceptably low.

### SUMMARY OF THE INVENTION

20 The present invention provides a fracturing fluid or crosslinking composition suitable for use at high temperature comprising (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to provide a pH of less than 9, (e) an organic acid, (f) hydroxypropyl guar and (g) a zirconium crosslinking agent. Preferably  
25 pH is from 7.5 to 8.9, more preferably from 8.0 to 8.9. Preferably the buffer is sodium carbonate or potassium carbonate. More preferably the buffer is sodium carbonate. The fracturing fluid is particularly suitable for use at high temperature, i.e., at temperatures of about  $275^\circ\text{F}$  ( $135^\circ\text{C}$ ) or higher, for example, at a temperature of  $275$ - $340^\circ\text{F}$  ( $135$ - $171^\circ\text{C}$ ).

30 The present invention further provides methods for using the fracturing fluid of this invention in oil field applications, for example, for

hydraulically fracturing a subterranean formation. The fracturing fluid of this invention is further useful for plugging permeable zones or leaks in subterranean formations.

### DETAILED DESCRIPTION OF THE INVENTION

5 Trademarks and tradenames are shown herein in upper case.

The present invention provides a fracturing fluid comprising HPG having sufficient viscosity for use in high temperature wells. Furthermore, sufficient viscosity is maintained for a sufficient time for treating a subterranean zone. More specifically, the present invention provides a  
10 fracturing fluid or cross-linking composition comprising (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to provide a pH of less than 9, (e) an organic acid, (f) hydroxypropyl guar and (g) a zirconium crosslinking agent. Each component is present in an amount sufficient to provide a viscosity of at  
15 least 100 centipoise (cp), 90 minutes after contacting the components a temperature of at least 275°F (135°C).

The aqueous liquid (a) is typically selected from the group consisting of water and aqueous alcohol. Preferably, the aqueous liquid is water, aqueous methanol or aqueous ethanol.

20 By brine (b), it is meant one or more components, preferably salts that act as clay stabilizers. Brine may comprise, for example, hydrochloric acid and chloride salts, such as, tetramethylammonium chloride (TMAC), sodium chloride or potassium chloride. Aqueous brine solutions may be used and comprise, for example, 0.5 to 5.0 weight % of the clay stabilizer,  
25 based on the total weight of the fracturing fluid. Preferably the brine is tetramethylammonium chloride or potassium chloride.

Thermal stabilizers (c) include, for example, methanol, alkali metal thiosulfate, and ammonium thiosulfate. Preferably the thermal stabilizer is an alkali metal thiosulfate, more preferably sodium thiosulfate. The  
30 concentration of thermal stabilizer in the fracturing fluid is 0.1 to 0.5

weight %, preferably 0.2 to 0.4 weight % of the thermal stabilizers based on the total weight of the fracturing fluid.

The fracturing fluid comprises an effective amount of a pH buffer (d), which is a non-delaying alkaline buffer, to control pH at a pH less than 9. By "non-delaying alkaline buffer" it is meant a buffer, which upon addition to the composition does not delay the rate of cross-linking. The preferred buffer is sodium carbonate or potassium carbonate, more preferred is sodium carbonate. Preferably pH is from 7.5 to 8.9, more preferably from 8.0 to 8.9. The fracturing fluid comprises 0.05 to 0.2 weight %, preferably 0.05 to 0.15 weight %, based on the total weight of the fracturing fluid.

The fracturing fluid comprises an organic acid (e). The organic acid is defined as a carboxylic acid. The preferred organic acids are formic acid, acetic acid, lactic acid and fumaric acid. Preferably the acid is fumaric acid. The fracturing fluid comprises 0.01 to 0.15 weight %, preferably 0.02% to 0.1 weight %, and most preferably 0.04 weight % to 0.08 weight % organic acid based on the total weight of the fracturing fluid.

The fracturing fluid comprises a cross-linkable organic polymer (f), which is hydroxypropyl guar (HPG). The fracturing fluid comprises 0.2 to 1.0 weight %, preferably 0.4 to 0.7 weight % of HPG, based on the total weight of the fracturing fluid.

The fracturing fluid comprises a zirconium crosslinking agent (g). The zirconium crosslinking agents are zirconium containing compounds that enable polymerization compounds to form three-dimensional networks. Examples of zirconium crosslinking agents include zirconium alkanolamine complex, zirconium alkanolamine polyol complex and salts of zirconium lactate, including sodium, ammonium and alkanolamine salt.

Zirconium alkanolamine complex may be prepared by reacting a tetraalkyl zirconate with alkanolamine. Zirconium alkanolamine polyol complex may be prepared by reacting a tetraalkyl zirconate with alkanolamine and a suitable polyol. The tetraalkyl zirconate is typically

expressed by the general formula  $Zr(OR)_4$  where each R is individually selected from an alkyl, cycloalkyl, alkaryl, hydrocarbyl radical containing from 1 to about 30, preferably 2 to about 18, and most preferably 2 to 12 carbon atoms per radical and each R can be the same or different. In

5 reaction of a tetraalkyl zirconate with alkanolamine, the alkanolamine replaces four of the OR groups in the tetraalkyl zirconate. Zirconium alkanolamine complex and zirconium alkanolamine polyol complex are commercially available, e.g., from E. I. du Pont de Nemours and Company, Wilmington, DE.

10 Zirconium lactate can be prepared by reacting a zirconium oxychloride with lactic acid. The reaction can be followed by neutralization with a base such as ammonia, an alkali metal hydroxide, alkanolamine or by reaction with a quaternary ammonium hydroxide. The preferred zirconium lactate salts are zirconium tris-ammonium lactate or its sodium  
15 salt analogue, zirconium tris-sodium lactate. Zirconium lactates are commercially available, e.g., from E. I. du Pont de Nemours and Company, Wilmington, DE.

Preferably the zirconium crosslinking agent is selected from the group consisting of alkanolamine complex, zirconium alkanolamine polyol  
20 complex, zirconium tris-ammonium lactate, and zirconium tris-sodium lactate.

The zirconium crosslinking agent is generally dissolved in an organic, aqueous or mixed aqueous/organic solvent, providing a zirconium solution. Typical solvents include water and alcohols, such as ethanol, n-  
25 propanol, and isopropanol.

The fracturing fluid comprises between 10 to 50 ppm ( $\mu\text{g/g}$ ), preferably 30-40 ppm zirconium (as Zr), based on the total weight of the fracturing fluid.

The fracturing fluid may comprise optional components, including  
30 those which are common additives for oil field applications. Thus, the fracturing fluid may further comprise one or more of proppants, friction

reducers, bactericides, organic solvents, chemical breakers, surfactants, formation control agents, and the like. Proppants include sand, bauxite, glass beads, nylon pellets, aluminum pellets and similar materials.

Friction reducers include polyacrylamides. Organic solvents that may be used include alcohols, glycols, polyols, and hydrocarbons such as diesel. Chemical breakers break the cross-linked polymer (gel) in a controlled manner and include enzymes, alkali metal persulfate, and ammonium persulfate.

These optional components are added in an effective amount sufficient to achieve the desired cross-linking performance based on the individual components, desired cross-linking time, temperature and other conditions present in the formation being fractured or permeable zone being plugged.

The fracturing fluid is prepared by a process comprising contacting the cross-linkable polymer (HPG), typically with mixing, with the aqueous liquid to form a base gel. The base gel and zirconium crosslinking agent are then contacted to provide the fracturing fluid. Other components, including optional components can be added to the base gel, the zirconium crosslinking agent or both.

While there is no particular order of addition that is required to prepare the fracturing fluid of the present invention, it may be convenient to first combine the aqueous liquid and brine to provide an aqueous brine. To the aqueous brine may be added simultaneously or sequentially the thermal stabilizer, acid and hydroxypropyl guar. By "simultaneous" addition, it is meant herein that two or more components are added at the same time or less than 60 seconds apart, for example, not more than 30 seconds apart. Typically, the aqueous liquid, brine, thermal stabilizer, acid, and hydroxypropyl guar are mixed and allowed to stand for a period of time, typically less than 60 minutes, preferably for 10-40 minutes, such as for 30 minutes, prior to adding the buffer. The buffer (preferably sodium carbonate or potassium carbonate) is added to the mixture and the mixture is allowed to stand for a period of time, typically less than 60

minutes, preferably for 10-40 minutes, such as for 30 minutes. prior to adding the zirconium crosslinking agent. The zirconium crosslinking agent is generally the final component added to the fracturing fluid.

This invention provides a method for hydraulically fracturing a subterranean formation, which comprises introducing into the formation at a flow rate and pressure sufficient to create, reopen, and/or extend one or more fractures in the formation, a fracturing fluid which comprises (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to provide a pH of less than 9, (e) an organic acid, (f) hydroxypropyl guar (HPG) and (g) a zirconium crosslinking agent. The preferred embodiments of the fracturing fluid are described hereinabove.

In one embodiment of the method for hydraulically fracturing a subterranean formation, the aqueous liquid, brine, thermal stabilizer, buffer, acid, hydroxypropyl guar, and the zirconium crosslinking agent are premixed and introduced into the subterranean formation as a single stream. In this embodiment, a zirconium crosslinking agent and HPG are contacted prior to their introduction into the formation, such that the crosslinking agent and HPG polymer react to form a crosslinked gel. Preferably, the zirconium crosslinking agent is introduced as a zirconium solution. The cross-linked gel is then introduced into the formation at a flow rate and pressure sufficient to create, reopen, and/or extend a fracture in the formation. In this method, a base gel is prepared by mixing HPG with the aqueous liquid. A crosslinked gel is prepared by mixing the base gel with a solution of the zirconium crosslinking agent (zirconium solution). In this embodiment, the additional components - the brine, thermal stabilizer, buffer, and acid, and any optional components, may be added to the base gel, the zirconium solution or both. For example, the HPG may be mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to provide the base gel. This base gel is mixed with the zirconium solution to produce a crosslinked gel, which is then introduced into the formation.

In a second embodiment of the method for hydraulically fracturing a subterranean formation, zirconium crosslinking agent and HPG are not contacted prior to their introduction into the formation. This method comprises (a) preparing a base gel by mixing HPG with an aqueous liquid; (b) introducing the base gel into the formation, (c) simultaneously with or sequentially after introducing the base gel into the formation, introducing the zirconium crosslinking agent into the formation; and (d) permitting the base gel and the crosslinking agent to react to form a crosslinked gel in the formation. Preferably, the zirconium crosslinking agent is introduced as a zirconium solution. The additional components - the brine, thermal stabilizer, buffer, and acid - and any optional components, can be added to the base gel, the zirconium crosslinking agent or both. For example, the HPG may be mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to provide the base gel. This base gel is mixed with the zirconium crosslinking agent in the formation to produce a crosslinked gel.

In an alternative when zirconium crosslinking agent and HPG are not contacted prior to their introduction into the subterranean formation, the formation is penetrated by a wellbore. A zirconium crosslinking agent, preferably in the form of a zirconium solution, is contacted with a base gel in the wellbore to form a crosslinked gel. The crosslinked gel is introduced into the formation from the wellbore. A zirconium solution is prepared by dissolving a zirconium crosslinking agent in a solvent such as water or an alcohol. This method of hydraulically fracturing a subterranean formation penetrated by a wellbore comprises (a) preparing a base gel by contacting hydroxypropyl guar with an aqueous liquid; (b) introducing the base gel into the wellbore; (c) simultaneously with or sequentially after introducing the base gel into the wellbore, introducing the zirconium crosslinking agent into the wellbore; (d) permitting the base gel and the zirconium crosslinking agent to react to form a crosslinked gel in the wellbore; and (e) introducing the crosslinked gel into the formation from the wellbore at a flow rate and pressure sufficient to create, reopen, and/or extend a

fracture in the formation. Additional components - the brine, thermal stabilizer, buffer, and acid – and any optional components, are independently admixed with the base gel, the zirconium crosslinking agent or both prior to introducing the base gel and the zirconium crosslinking agent into the wellbore. For example, the HPG may be mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to provide the base gel. This base gel is mixed with the zirconium crosslinking agent to produce a crosslinked gel, which is then introduced into the formation.

Upon creation of a fracture or fractures, the method may further comprise introducing a fracturing fluid comprising a zirconium crosslinking agent, a cross-linkable organic polymer and proppant into the fracture or fractures. This second introduction of zirconium is preferably performed in the event the cross-linking composition used to create the fracture or fractures did not comprise proppant. The cross-linkable organic polymer in this second addition may be hydroxypropyl guar or any other suitable cross-linkable organic polymer.

This invention further provides a method for selectively plugging permeable zones and leaks in subterranean formations, which comprises introducing into the permeable zone or the site of the subterranean leak, a fracturing fluid comprising (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to provide a pH of less than 9, (e) an organic acid, (f) hydroxypropyl guar and (g) a zirconium crosslinking agent. Optional components as described hereinabove, can be added to the fracturing fluid prior to introducing the fracturing fluid into the permeable zone or site of the leak.

In one embodiment of the method for plugging a permeable zone or a leak in a subterranean formation, the aqueous liquid, brine, thermal stabilizer, buffer, acid, hydroxypropyl guar, and the zirconium crosslinking agent are premixed and introduced into the subterranean formation as a single stream. In this embodiment, a zirconium crosslinking agent and HPG are contacted prior to their introduction into the subterranean formation, such that the HPG polymer and zirconium crosslinking agent

react to form a crosslinked gel. Preferably, the zirconium crosslinking agent is introduced as a zirconium solution. The crosslinked gel is then introduced into the formation. In this method, a base gel is prepared by mixing HPG with the aqueous liquid. A crosslinked gel is prepared by  
5 mixing the base gel with a zirconium crosslinking agent (preferably as a zirconium solution). In this embodiment, the additional components - the brine, thermal stabilizer, buffer, and acid, and any optional components, may be added to the base gel, the zirconium crosslinking agent or both. For example, the HPG may be mixed with the aqueous liquid, brine,  
10 thermal stabilizer, buffer and acid to provide the base gel. This base gel is mixed with the zirconium crosslinking agent to produce a crosslinked gel, which is then introduced into the formation.

In a second embodiment of the method for plugging a permeable zone or a leak in a subterranean formation, zirconium crosslinking agent and HPG are not contacted prior to their introduction into the formation  
15 and crosslinking occurs within the subterranean formation. Preferably, the zirconium crosslinking agent is introduced as a zirconium solution. This method comprises (a) preparing a base gel by mixing HPG with an aqueous liquid; (b) introducing the base gel into the into the permeable  
20 zone or the site of the subterranean leak, (c) simultaneously with or sequentially after introducing the base gel into the into the permeable zone or the site of the subterranean leak, introducing the zirconium crosslinking agent into the permeable zone or the site of the subterranean leak; and  
25 (d) permitting the base gel and the crosslinking agent to react to form a crosslinked gel to plug the zone and/or leak. In this embodiment, the additional components - the brine, thermal stabilizer, buffer, and acid – and any optional components, can be added to the base gel, with the zirconium crosslinking agent, or both. For example, the HPG may be mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to  
30 provide the base gel. This base gel is mixed with the zirconium crosslinking agent in the formation to produce a crosslinked gel.

In an alternative when zirconium crosslinking agent and HPG are not contacted prior to their introduction into the permeable zone or the leak in a subterranean formation, the zone or formation is penetrated by a wellbore. A zirconium crosslinking agent, preferably in the form of a zirconium solution, is contacted with a base gel in the wellbore to form a crosslinked gel. The crosslinked gel is introduced into the formation from the wellbore. A zirconium solution is prepared by dissolving a zirconium crosslinking agent in a solvent such as water or an alcohol. This method of plugging a permeable zone or a leak in a subterranean formation, wherein the zone or leak is penetrated by a wellbore comprises (a) preparing a base gel by mixing hydroxypropyl guar with an aqueous liquid; (b) introducing the base gel into the wellbore; (c) simultaneously with or sequentially after introducing the base gel into the wellbore, introducing a zirconium crosslinking agent into the wellbore; (d) permitting the base gel and the zirconium crosslinking agent to react to form a crosslinked gel in the wellbore; and (e) introducing the crosslinked gel from the wellbore into the zone or formation. Additional components - the brine, thermal stabilizer, buffer, and acid – and any optional components, are independently admixed with the base gel, the zirconium crosslinking agent or both prior to introducing the base gel and the zirconium crosslinking agent into the wellbore. For example, the HPG may be mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to provide the base gel. This base gel is mixed with the zirconium crosslinking agent to produce a crosslinked gel in the wellbore, which is then introduced into the formation.

The relative amounts of HPG and the zirconium crosslinking agent complex may vary. One uses small but effective amounts which for both will vary with the conditions, e.g., the type of subterranean formation, the depth at which the method (e.g., fluid fracturing, permeable zone plugging or leak plugging) is to be performed, temperature, pH, etc. Generally one uses as small an amount of each component as will provide the viscosity level necessary, such as a viscosity of at least 100 cp at 90 minutes after

forming the crosslinked gel to effect the desired result, i.e., fracturing of the subterranean formation, or plugging permeable zones or leaks to the extent necessary to promote adequate recovery of oil or gas from the formation.

- 5 Surprisingly, addition of acid to a base gel for a fracturing fluid and maintaining pH at less than 9 using an alkaline buffer, allows HPG to be used as cross-linkable organic polymer at a temperature of about 275°F (135°C) or higher in a method for hydraulically fracturing a subterranean formation or in a method for selectively plugging permeable zones or leaks  
10 in subterranean formations.

### EXAMPLES

- The zirconium crosslinkers, zirconium lactate sodium salt (TYZOR 217 organic zirconate), alkanolamino zirconate (TYZOR 212 organic zirconate) and triethanolamino zirconate (TYZOR TEAZ organic  
15 zirconate), are all commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE. Zirconium lactate ammonium salt was made by reacting zirconium oxychloride with lactic acid, followed by neutralization with ammonium hydroxide.

- Carboxymethylhydroxypropylguar (CMHPG), hydroxypropylguar  
20 (HPG) and natural guar are commercially available from Rhodia, Inc., NJ. All other chemicals used herein were purchased from Aldrich Chemical Company, Milwaukee, WI.

#### Comparative Examples A1 and A2

- A base gel was prepared by adding distilled water (1L) to a Waring  
25 blender jar and KCl brine (20 g). The solution was agitated and hydroxypropylguar (HPG, 4.2 g) was added to the vortex of the agitating solution. The solution was agitated for 30 minutes. Sodium bicarbonate buffer (1.45 g) and sodium thiosulfate pentahydrate (1.2 g) were added to the solution. The solution was mixed for 30 minutes. The resulting gel  
30 was allowed to stand for at least one hour prior to adding zirconium crosslinker to produce a fracturing fluid.

### Comparative Example B

A base gel was prepared by adding distilled water (1L) to a Waring blender jar and sodium thiosulfate pentahydrate (3.6 g). The solution was agitated and hydroxypropyl guar (HPG, 6.6 g) was added to the vortex of the agitating solution. The solution was agitated for 30 minutes. Sodium carbonate buffer was added to adjust pH to 9.5. Then sodium hydroxide was added to adjust pH to 10. The solution was agitated for 5 minutes and citric acid water solution (25%, 0.75g) was added. The solution was agitated for 5 minutes. The resulting gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

### Comparative Examples C1 and D1

A base gel was prepared by adding distilled water (1L) to a Waring blender jar and a 50% aqueous solution of tetramethylammonium chloride brine (TMAC, 2 g). The solution was agitated and carboxymethylhydroxypropyl guar (CMHPG, 6 g) was sprinkled into the vortex of the agitating solution. The pH of the resultant slurry was adjusted to 6 with sodium diacetate (buffer) and agitated for 30 minutes. The pH was then adjusted to 10 with 10% sodium hydroxide solution. Agitation was stopped and the gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

### Comparative Examples C2 and D2

A base gel was prepared by adding distilled water (1L) to a Waring blender jar and a 50% aqueous solution of tetramethylammonium chloride brine (2 g) was added. The solution was agitated and hydroxypropyl guar (HPG, 6 g) was added to the vortex of the agitating solution. The pH of the resultant slurry was adjusted to 6 with sodium diacetate and agitated for 30 minutes. The pH was then adjusted to 10 with sodium hydroxide solution (10%). The gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

### Comparative Example E

A base gel was prepared by adding distilled water (1L) to a Waring blender jar and KCl brine (20 g) was added. The solution was agitated. Sodium thiosulfate pentahydrate (2.4 g), fumaric acid (0.55 g) and natural guar (6.0 g) were added to the solution and the solution was agitated for 5 30 minutes. The pH was then adjusted to pH 8.8 with sodium carbonate (buffer). The agitation was stopped and the gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

#### Examples 1-5

10 A base gel was prepared by adding distilled water (1L) to a Waring blender jar and KCl brine (20 g) was added. The solution was agitated. Sodium thiosulfate pentahydrate (2.4 g), fumaric acid (0.55 g) and hydroxypropyl guar (HPG, 6.0 g) were added to the solution simultaneously (i.e., less than 60 seconds for the addition) and the 15 solution was agitated for 30 minutes. The pH was then adjusted to pH 7.8-8.8 with sodium carbonate (buffer). The agitation was stopped and the gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

#### Example 6

20 A base gel was prepared by adding distilled water (1L) to a Waring blender jar and KCl brine (20 g) was added. The solution was agitated. Sodium thiosulfate pentahydrate (2.4 g), acetic acid (0.58 g) and hydroxypropyl guar (HPG, 6.0 g) were added to the solution and the solution was agitated for 30 minutes. The pH was then adjusted to pH 8.8 25 with sodium carbonate (buffer). The agitation was stopped and the gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

#### Example 7

A base gel was prepared by adding distilled water (1L) to a Waring 30 blender jar and KCl brine (20 g) was added. The solution was agitated. Sodium thiosulfate pentahydrate (2.4 g), lactic acid (0.76 g) and

- hydroxypropyl guar (HPG, 6.0 g) were added to the solution and the solution was agitated for 30 minutes. The pH was then adjusted to pH 8.8 with sodium carbonate (buffer). The agitation was stopped and the gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

#### Example 8

- A base gel was prepared by adding distilled water (1L) to a Waring blender jar and KCl brine (20 g) was added. The solution was agitated. Sodium thiosulfate pentahydrate (2.4 g), formic acid (0.44 g) and hydroxypropyl guar (HPG, 6.0 g) were added to the solution and the solution was agitated for 30 minutes. The pH was then adjusted to pH 8.8 with sodium carbonate (buffer). The agitation was stopped and the gel was allowed to stand for 30 minutes prior to adding zirconium crosslinker to produce a fracturing fluid.

#### Viscosity measurement of zirconate cross-linked base gels

- After preparation of base gels, the desired amount of zirconium crosslinker (32-148 ppm) was added to each base gel (250 ml) and the resulting solution was then agitated for 30 seconds. The fracturing fluid, i.e., agitated base gel containing crosslinker (25 ml), was placed into the cup of the FANN 50 Viscometer, unless the fracturing had gelled in the blender. The viscosity was measured at a continuous shear rate of 170 reciprocal seconds of shear and between 275-340°F (135-171°C). Viscosity measurements were recorded after 10, 30, 60 and 90 minutes when possible.

Table 1. Performance Results

| Example  | Zr complex                   | Guar type<br>/strength<br>(weight %) | Acid            | Brine | Zr, ppm | Temp.<br>°F (°C) | pH  | Viscosity, cp     |            |            |         |            |
|----------|------------------------------|--------------------------------------|-----------------|-------|---------|------------------|-----|-------------------|------------|------------|---------|------------|
|          |                              |                                      |                 |       |         |                  |     | Maximum           | 10<br>min. | 30<br>min. | 60 min. | 90<br>min. |
| Comp. A1 | Zirconium<br>lactate-Na      | HPG/35<br>(0.42)                     |                 | KCl   | 32      | 275<br>(135)     | 8.5 | 170               | 90         | -          | -       | -          |
| Comp. A2 | Zirconium<br>lactate-Na      | HPG/35<br>(0.42)                     |                 | KCl   | 54      | 340<br>(171)     | 8.5 | 330               | 30         | -          | -       | -          |
| Comp. B  | Zirconium<br>lactate-Na      | HPG/55<br>(0.66)                     |                 | KCl   | 32      |                  | 10  | Gelled in blender |            |            |         |            |
| Comp. C1 | Alkanolamino<br>zirconate    | CMHPG/50<br>(0.60)                   |                 | TMAC  | 148     | 300<br>(149)     | 10  | 2500              | 1270       | 850        | 500     | 250        |
| Comp. C2 | Alkanolamino<br>zirconate    | HPG/50<br>(0.60)                     |                 | TMAC  | 148     | 250<br>(121)     | 10  | 520               | 30         | -          | -       | -          |
| Comp. D1 | Triethanolamino<br>zirconate | CMHPG/50<br>(0.60)                   |                 | TMAC  | 68      | 300<br>(149)     | 10  | 2100              | 1370       | 490        | 130     | -          |
| Comp. D2 | Triethanolamino<br>zirconate | HPG/50<br>(0.60)                     |                 | TMAC  | 68      | 275<br>(135)     | 10  | 810               | 20         | -          | -       | -          |
| Comp. E  | Zirconium<br>lactate-Na      | Natural<br>guar/50<br>(0.60)         | Fumaric<br>acid | KCl   | 32      |                  | 8.8 | Gelled in blender |            |            |         |            |

Table 2. Performance Results

| Example | Zr complex                | Guar type<br>/strength<br>(weight %) | Acid            | Brine | Zr, ppm | Temp.<br>°F (°C) | pH  | Viscosity, cp |            |            |            |            |
|---------|---------------------------|--------------------------------------|-----------------|-------|---------|------------------|-----|---------------|------------|------------|------------|------------|
|         |                           |                                      |                 |       |         |                  |     | Maximum       | 10<br>min. | 30<br>min. | 60<br>min. | 90<br>min. |
| 1       | Alkanolamino<br>zirconate | HPG/50<br>(0.60)                     | Fumaric<br>acid | KCl   | 37      | 300<br>(149)     | 8.8 | 600           | 417        | 240        | 159        | 140        |
| 2       | Zirconium<br>lactate-Na   | HPG/50<br>(0.60)                     | Fumaric<br>acid | KCl   | 32      | 275<br>(135)     | 7.8 | 270           | 220        | 190        | 170        | 130        |
| 3       | Zirconium<br>lactate-NH4  | HPG/50<br>(0.60)                     | Fumaric<br>acid | KCl   | 36      | 300<br>(149)     | 8.8 | 418           | 322        | 298        | 272        | 258        |
| 4       | Zirconium<br>lactate-Na   | HPG/50<br>(0.60)                     | Fumaric<br>acid | KCl   | 32      | 340<br>(171)     | 8.8 | 781           | 505        | 266        | 150        | 112        |
| 5       | Zirconium<br>lactate-NH4  | HPG/50<br>(0.60)                     | Fumaric<br>acid | KCl   | 30      | 340<br>(171)     | 8.8 | 458           | 208        | 135        | 112        | 105        |
| 6       | Zirconium<br>lactate-Na   | HPG/50<br>(0.60)                     | Acetic<br>acid  | KCl   | 32      | 300<br>(149)     | 8.8 | 918           | 538        | 380        | 288        | 268        |
| 7       | Zirconium<br>lactate-Na   | HPG/50<br>(0.60)                     | Lactic<br>acid  | KCl   | 32      | 300<br>(149)     | 7.8 | 752           | 620        | 361        | 200        | 154        |
| 8       | Zirconium<br>lactate-Na   | HPG/50<br>(0.60)                     | Formic<br>acid  | KCl   | 32      | 300<br>(149)     | 8.8 | 718           | 418        | 370        | 337        | 310        |

## Results

Tables 1 and 2 provide Performance Results for Comparative Examples and Examples of this invention. Tables 1 and 2 list the zirconium crosslinker type, guar type and strength, brine used, the organic acid, when used, temperatures, pH, and measured viscosity results for each of the Comparative Examples and Examples of this invention. Guar strength is measured in pptg (lbs per 1000 gal), and in weight % in parentheses. "Zr loading" refers to the amount of zirconium added in parts per million (ppm) based on the total weight of the fracturing fluid. The viscosity measurements are measured in centipoise (cp) at time interval indicated. Zirconium crosslinked base gels perform well if the gel remains at acceptable viscosity levels for 90 minutes, for example, greater than 100 cp. Zirconium cross-linked gels are considered "failed" if viscosity is less than 100 cp after 90 minutes or if viscosity is listed as "-", indicating the viscosity was so low that the gel degraded during the measurements (prior to the 90 minutes). Alternatively, the fracturing fluids failed if the fracturing fluid gelled prior to measuring viscosity (i.e. Table recites, "Gelled in blender").

Comparative Examples A1 and A2 were base gels cross-linked with zirconium lactate, also referred to as fracturing fluids, prepared using conditions described in US Patent 4,801,389. The fracturing fluid had an initial high viscosity but after 10 minutes, the viscosity was lower than desired and the fracturing fluid failed before 20 minutes. The fracturing fluids of Comparative Examples A1 and A2 failed at 275°F (135°C) and 340°F 171°C), respectively.

A base gel cross-linked with zirconium lactate prepared according to US Patent 6,737,386, but using HPG rather than natural guar, was used in Comparative Example B. The fracturing fluid gelled immediately, so no viscosity measurements. Surprisingly, the conditions which worked for

natural guar in U.S. Patent 4,801,389 or 6,737,386 were not effective when natural guar was replaced with the derivatized guar, HPG.

5 A base gel cross-linked with zirconium lactate prepared using conditions in this invention using natural guar in place of HPG, was used in Comparative Example E. Surprisingly, the crosslinking composition gelled immediately.

Comparative Examples C1 and C2 were base gels prepared using CMHPG and HPG, respectively, and cross-linked with alkanolamine zirconate to produce fracturing fluids. The CMHPG-fluid performed well at  
10 high temperatures through 90 minutes, but the HPG-fluid showed low viscosity at 10 minutes and failed at 250°F. Thus, when it is desirable to use HPG rather than CMHPG, or if CMHPG is not available, conditions that work for CMHPG cannot always be used successfully with HPG.

Comparative Examples D1 and D2 were base gels prepared using  
15 CMHPG and HPG, respectively, and cross-linked with triethanolamine zirconate to produce fracturing fluids. The CMHPG-fluid performed well at high temperatures through 60 minutes, but the HPG-fluid showed failed after 10 minutes at 275°F (135°C). Again, these Comparative Examples show HPG and CMHPG are not interchangeable in fracturing fluids.

20 Examples 1-8, fracturing fluids of this invention, were prepared using HPG and zirconium lactate sodium salt, zirconium lactate ammonium salt and alkanolamino zirconate at temperatures between 275 and 340°F (135 and 171°C). Examples 1-8 exhibited desirable viscosities over the 90 minute time period (viscosity of greater than 100 cp after 90  
25 minutes) and did not show premature degradation caused by shearing as shown in Comparative Examples using HPG. Viscosity and maintenance of viscosity over time, using HPG in the fracturing fluids of this invention were comparable to each other at the high temperatures of the tests and comparable to Comparative Examples that used CMHPG in fracturing  
30 fluids using triethanolamine zirconates.

Thus, it has been shown that fracturing fluids of this invention comprising zirconium crosslinking agent, brine (KCl), a stabilizer, a non-delayed alkaline buffer (sodium carbonate), an acid, a pH less than 9, and a temperature in the range of 275-340°F (135-171°C) are useful as the

5   hydraulic fracturing fluids. These fracturing fluids may be used in the field for fracturing or plugging of deep, hot wells in areas where HPG is the predominant guar used.

PCT CLAIMSWhat is claimed is:

1. A fracturing fluid comprising (a) an aqueous liquid, (b) brine,  
(c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to  
5 provide a pH less than 9, (e) an organic acid, (f) hydroxypropyl guar and  
(g) a zirconium crosslinking agent.
2. The fracturing fluid of claim 1 wherein the pH is from 7.5 to  
8.9.
3. The fracturing fluid of claim 1 wherein the aqueous liquid is  
10 selected from the group consisting of water and aqueous alcohol.
4. The fracturing fluid of claim 1 wherein the buffer is sodium  
carbonate or potassium carbonate.
5. The fracturing fluid of claim 4 wherein the brine is  
tetramethylammonium chloride or potassium chloride; the thermal  
15 stabilizer is methanol, alkali metal thiosulfate or ammonium thiosulfate; the  
acid is formic acid, acetic acid, lactic acid or fumaric acid.
6. The fracturing fluid of claim 5 wherein the aqueous liquid is  
water, the thermal stabilizer is sodium thiosulfate, the buffer is sodium  
carbonate and the acid is fumaric acid.
- 20 7. A method for hydraulically fracturing a subterranean  
formation comprising introducing into a subterranean formation at a flow  
rate and pressure sufficient to create, reopen and/or extend a fracture in  
the formation, (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a

non-delaying alkaline buffer sufficient to provide a pH less than 9, (e) an organic acid, (f) hydroxypropyl guar and (g) a zirconium crosslinking agent wherein the temperature of the formation is in the range of 275-340°F (135-171°C).

5           8.       The method of claim 7 wherein the aqueous liquid, brine, thermal stabilizer, buffer, acid, hydroxypropyl guar, and the zirconium crosslinking agent are premixed and introduced into the subterranean formation as a single stream.

          9.       The method of claim 7 wherein the subterranean formation is  
10   penetrated by a wellbore; and the process comprises (a) preparing a base gel by contacting hydroxypropyl guar with an aqueous liquid; (b) introducing the base gel into the wellbore; (c) simultaneously with or sequentially after introducing the base gel into the wellbore, introducing the zirconium crosslinking agent into the wellbore; (d) permitting the base  
15   gel and the zirconium crosslinking agent to react to form a crosslinked gel in the wellbore; and (e) introducing the crosslinked gel into the formation from the wellbore at a flow rate and pressure sufficient to create, reopen, and/or extend a fracture in the formation.

          10.      The method of claim 9 wherein the zirconium crosslinking  
20   agent is in the form of a zirconium solution, which is prepared by dissolving the zirconium crosslinking agent in water or an alcohol and wherein the hydroxypropyl guar is mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to provide the base gel.

11. A method for plugging a permeable zone or leak in a subterranean formation comprising introducing into said zone or said leak, (a) an aqueous liquid, (b) brine, (c) a thermal stabilizer, (d) a non-delaying alkaline buffer sufficient to provide a pH less than 9, (e) an organic acid, (f) hydroxypropyl guar and (g) a zirconium crosslinking agent wherein the temperature of the zone or formation is in the range of 275-340°F (135-171°C).

12. The method of claim 11 wherein the aqueous liquid, brine, thermal stabilizer, buffer, acid, hydroxypropyl guar, and the zirconium crosslinking agent are premixed and introduced into the subterranean formation as a single stream.

13. The method of claim 11 wherein the zirconium crosslinking agent and hydroxypropyl guar are not contacted prior to their introduction into the formation and wherein the zone or formation is penetrated by a wellbore comprising (a) preparing a base gel by mixing hydroxypropyl guar with an aqueous liquid; (b) introducing the base gel into the wellbore; (c) simultaneously with or sequentially after introducing the base gel into the wellbore, introducing a zirconium crosslinking agent into the wellbore; (e) permitting the base gel and the zirconium crosslinking agent to react to form a crosslinked gel in the wellbore; and (f) introducing the crosslinked gel from the wellbore into the zone or formation.

14. The method of claim 13 wherein the zirconium crosslinking agent is in the form of a zirconium solution, which is prepared by dissolving the zirconium crosslinking agent in water or an alcohol and

wherein the hydroxypropyl guar is mixed with the aqueous liquid, brine, thermal stabilizer, buffer and acid to provide the base gel.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/082024

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/512 C09K8/60 C09K8/68

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

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                       | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 4 883 605 A (PUTZIG DONALD E [US])<br>28 November 1989 (1989-11-28)<br>column 1, line 14 - line 18<br>column 2, line 16 - line 32<br>column 4, line 8 - line 11; example 1;<br>table 1<br>column 4, line 19 - line 22 | 1-14                  |
| A         | EP 0 302 544 A (PUMPTech NV [BE];<br>SCHLUMBERGER CIE DOWELL [FR])<br>8 February 1989 (1989-02-08)<br>cited in the application<br>table 1; compound 1<br>-----<br>-/--                                                   | 1-14                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

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- \*G\* document member of the same patent family

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Redecker, Michael

## INTERNATIONAL SEARCH REPORT

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PCT/US2008/082024

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                     | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 4 578 488 A (RUMMO GREGORY J [US] ET AL) 25 March 1986 (1986-03-25)<br>column 1, line 10 - line 24<br>column 3, line 1 - line 22; examples 1,2,5,6<br>-----                                                                                                         | 1-14                  |
| A         | US 4 692 254 A (KUCERA CLARE H [US]) 8 September 1987 (1987-09-08)<br>column 1, line 12 - line 16<br>column 5, line 50 - line 61<br>column 6, line 14 - line 32<br>column 7, line 20 - column 8, line 20;<br>table 2<br>column 9, line 6 - column 10, line 45<br>----- | 1-14                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2008/082024

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date                                                                                                                  |
|-------------------------------------------|---------------------|----------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| US 4883605                                | A                   | 28-11-1989                 | NONE                                                                                                                                 |
| EP 0302544                                | A                   | 08-02-1989                 | CA 1280588 C 26-02-1991<br>DE 3871642 D1 09-07-1992<br>DE 3871642 T2 10-12-1992<br>NO 883427 A 06-02-1989<br>US 4801389 A 31-01-1989 |
| US 4578488                                | A                   | 25-03-1986                 | NONE                                                                                                                                 |
| US 4692254                                | A                   | 08-09-1987                 | NONE                                                                                                                                 |