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(54) **Title**: CLEAN VISCOSIFIED TREATMENT FLUIDS AND ASSOCIATED METHODS

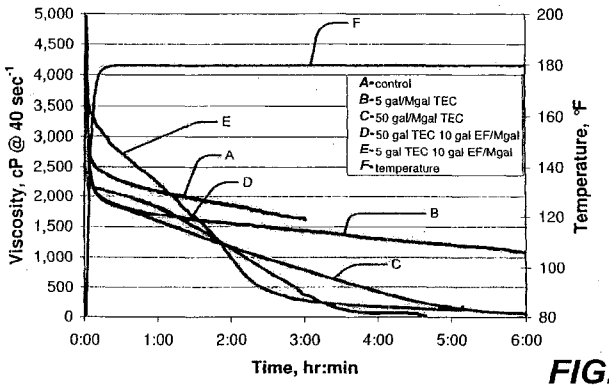


FIG. 1

(57) **Abstract**: Treatment fluids comprising an aqueous base fluid, a viscosifying agent, and a compliant dual- functional additive are provided. The present invention provides methods of using the treatment fluids in subterranean formations. One example of a suitable method includes providing a fracturing fluid comprising an aqueous base fluid, a viscosifying agent, and a compliant dual- functional additive that acts as a fluid loss control agent and a breaker and introducing the fracturing fluid into at least a portion of a subterranean formation at a rate and pressure sufficient to create or enhance at least one or more fractures in the subterranean formation.

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CLEAN VISCOSIFIED TREATMENT FLUIDS AND ASSOCIATED METHODS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to fluids useful for subterranean operations, and more particularly, to treatment fluids comprising a compliant dual-functional additive and a viscosifying agent, and methods of use employing such treatment fluids to treat subterranean formations.

[0002] Aqueous treatment fluids may be used in a variety of subterranean treatments. Such treatments include, but are not limited to, stimulation operations and completion operations. As used herein, the term "treatment," or "treating," refers to any subterranean operation that uses a fluid in conjunction with a desired function and/or for a desired purpose. The term "treatment," or "treating," does not imply any particular action by the fluid.

[0003] An example of a subterranean treatment using an aqueous treatment fluid is hydraulic fracturing. In a hydraulic fracturing treatment, a viscous fracturing fluid is introduced into the formation at a high enough rate to exert a sufficient pressure on the formation to create and/or extend fractures therein. The viscous fracturing fluid suspends proppant particles that are to be placed in the fractures to prevent the fractures from fully closing (once the hydraulic pressure is released), thereby forming conductive channels within the formation through which hydrocarbons can flow toward the well bore for production. In certain circumstances, a portion of the fracturing fluid may be lost during the fracturing operation, *e.g.*, through undesirable leakoff into natural fractures present in the formation. Typically, operators have attempted to solve this problem by including a fluid loss control additive in the fracturing fluid. Many conventional fluid loss control additives permanently reduce the permeability of a subterranean formation, negatively affect the rheology of the treatment fluid in which they are used, and/or reduce the rate at which the fluid is allowed to penetrate or leak off into desirable locations within the subterranean formation. Moreover, while it may be desirable to control or prevent fluid loss for a given period of time, in some instances it may become desirable to later allow a treatment fluid to penetrate or leak off into that portion of the subterranean formation. Thus, costly and time-consuming operations may be required to reverse the effects of conventional fluid loss control additives on the treatment fluid and/or to restore permeability to those portions of the subterranean formation affected by the fluid loss control additives.

[0004] Once at least one fracture is created and at least a portion of the proppant is substantially in place, the viscosity of the treatment fluid may be reduced, to facilitate removal

from the formation. This viscosity reduction or conversion is referred to as "breaking" and can be accomplished by incorporating chemical agents, referred to as "breakers," into the initial gel. Common breakers include oxidants or enzymes that operate to degrade the polymeric gel structure of the viscous treatment fluids. Common oxidizing agents used as breakers include persulfate salts (either used as is or encapsulated), organic peroxides, or alkaline earth and zinc peroxide salts. The timing of the break is also of great importance. Gels that break prematurely can lead to a premature reduction in the fluid viscosity, resulting in a less than desirable fracture width in the formation causing excessive injection pressures and premature termination of the treatment. On the other hand, gelled fluids that break too slowly can cause slow recovery of the fracturing fluid from the produced fracture with attendant delay in resuming the production of formation fluids and severely impair anticipated hydrocarbon production.

[0005] Numerous additives are used in the art to help control fluid loss or to break the viscosity of a treatment fluid in subterranean operations. However, the use of these conventional additives may give rise to other problems. First, the necessity of both a fluid loss control additive and a separate breaker additive in a treatment fluid may increase the complexity and cost of a treatment fluid and/or a subterranean application using that fluid. In some instances, the fluid loss control additives and breaker additives used are toxic and thus may harm the environment; this problem may be aggravated because many are poorly degradable or nondegradable within the environment. Due to environmental regulations, costly procedures often must be followed to dispose of the treatment fluids containing such compounds, ensuring that they do not contact the marine environment and groundwater. Thus, it is desirable to use low environmental impact additives for treatment fluids. It would also be desirable to reduce the number of additives needed in a treatment fluid.

SUMMARY OF THE INVENTION

[0006] The present invention relates to fluids useful for subterranean operations, and more particularly, to treatment fluids comprising a compliant dual-functional additive and a viscosifying agent, and methods of use employing such treatment fluids to treat subterranean formations.

[0007] According to one aspect of the present invention, there is provided a method comprising: providing a treatment fluid comprising an aqueous base fluid, a viscosifying agent, and a dual-functional additive that acts as a fluid loss control agent and a breaker; and introducing the treatment fluid into at least a portion of the subterranean formation.

Advantageously, the dual-function additive is a compliant dual-function additive. In an embodiment, the dual-functional additive restricts the flow of a fluid through pore throats within the subterranean formation.

[0008] In an embodiment, the dual-functional additive comprises an ester selected from the group consisting of: ethyl formate, propyl formate, butyl formate, amyl formate, anisyl formate, methyl acetate, propyl acetate, triacetin, butyl propionate, isoamyl propionate, ethyl lactate, methyl butyrate, ethyl isobutyrate, butyl isobutyrate, diethyl malonate, butyl ethyl malonate, dimethyl succinate, diethyl succinate, diethyl malate, diethyl tartrate, dimethyl tartrate, triethyl citrate, and any combination thereof.

[0009] In an embodiment, the dual-functional additive degrades to form an acid, and the acid acts as a viscosity reducing agent for the treatment fluid.

[0010] In an embodiment, the acid is selected from the group consisting of: formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, malonic acid, succinic acid, malic acid, tartaric acid, citric acid, and any combination thereof.

[0011] In an embodiment, the viscosifying agent is selected from the group consisting of: a carboxymethylguar, a carboxymethylhydroxyethylguar, a carboxymethylhydroxypropylguar, a hydroxyethyl cellulose, a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, diutan gum, a xanthan gum, a galactomannan, a cellulose derivative, a hydroxyethylguar, a hydroxypropylguar, a scleroglucan, a wellan, a starch, an acrylamide, an acrylate and any derivative and combination thereof.

[0012] In an embodiment, the viscosifying agent is crosslinked.

[0013] In an embodiment, a self-degrading filter cake is formed.

[0014] According to another aspect of the present invention, there is provided a method comprising: providing a fracturing fluid comprising an aqueous base fluid, a viscosifying agent, and a dual-functional additive that acts as a fluid loss control agent and a breaker; and introducing the treatment fluid into at least a portion of a subterranean formation at a rate and pressure sufficient to create or enhance at least one or more fractures in the subterranean formation. Advantageously, the dual-function additive is a compliant dual-function additive.

[0015] In an embodiment, the dual-functional additive comprises an ester selected from the group consisting of: ethyl formate, propyl formate, butyl formate, amyl formate, anisyl formate, methyl acetate, propyl acetate, triacetin, butyl propionate, isoamyl propionate, ethyl lactate, methyl butyrate, ethyl isobutyrate, butyl isobutyrate, diethyl malonate, butyl ethyl

malonate, dimethyl succinate, diethyl succinate, diethyl malate, diethyl tartrate, dimethyl tartrate, triethyl citrate, and any combination thereof.

[0016] In an embodiment, the dual-functional additive degrades to form an acid, and the acid acts as a viscosity reducing agent for the fracturing fluid.

[0017] In an embodiment, the acid is selected from the group consisting of: formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, malonic acid, succinic acid, malic acid, tartaric acid, citric acid, and any combination thereof.

[0018] In an embodiment, the viscosifying agent is selected from the group consisting of: a carboxymethylguar, a carboxymethylhydroxyethylguar, a carboxymethylhydroxypropylguar, a hydroxyethylcellulose, a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, diutan gum, a xanthan gum, a galactomannan, a cellulose derivative, a hydroxyethylguar, a hydroxypropylguar, scleroglucan, a wellan, a starch, an acrylamide, an acrylate and any derivative and combination thereof.

[0019] In an embodiment, the viscosifying agent is crosslinked.

[0020] According to another aspect of the present invention, there is provided a method comprising: providing a treatment fluid comprising an aqueous base fluid, a viscosifying agent, and a dual-functional additive that comprises a fluid loss control agent and a breaker; introducing the treatment fluid into at least a portion of the subterranean formation; and allowing the dual-functional additive to minimize fluid loss by obstructing at least one pore throat opening in the subterranean formation. Advantageously, the dual-function additive is a compliant dual-function additive.In an embodiment, the dual-functional additive comprises an ester selected from the group consisting of: ethyl formate, propyl formate, butyl formate, amyl formate, anisyl formate, methyl acetate, propyl acetate, triacetin, butyl propionate, isoamyl propionate, ethyl lactate, methyl butyrate, ethyl isobutyrate, butyl isobutyrate, diethyl malonate, butyl ethyl malonate, dimethyl succinate, diethyl succinate, diethyl malate, diethyl tartrate, dimethyl tartrate, triethyl citrate, and any combination thereof.

[0021] In an embodiment, the dual-functional additive releases an acid and the acid interacts with the viscosifying agent so as to reduce the viscosity of the treatment fluid.

[0022] In an embodiment, the acid is selected from the group consisting of: formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, malonic acid, succinic acid, malic acid, tartaric acid, citric acid, and any combination thereof.

[0023] In an embodiment, the viscosifying agent is selected from the group consisting of: a carboxymethylguar, a carboxymethylhydroxyethylguar, a

carboxymethylhydroxypropylguar, a hydroxyethylcellulose, a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, diutan gum, a xanthan gum, a galactomannan, a cellulose derivative, a hydroxyethylguar, a hydroxypropylguar, a scleroglucan, a wellan, a starch, an acrylamide, an acrylate and any derivative and combination thereof.

[0024] In an embodiment, a self-degrading filter cake is formed.

[0025] Other features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] These drawings illustrate certain aspects of some of the embodiments of the present invention, and should not be used to limit or define the invention.

[0027] Figure 1 shows the effect of triethyl citrate (TEC) with and without ethyl formate (EF) on the viscosity of the treatment fluid.

[0028] Figure 2 shows the dynamic fluid loss of the treatment fluid with and without triethyl citrate.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0029] The present invention relates to fluids useful for subterranean operations, and more particularly, to treatment fluids comprising a compliant dual-functional additive and a viscosifying agent, and methods of use employing such treatment fluids to treat subterranean formations.

[0030] The treatment fluids of the present invention may comprise a compliant dual-functional additive that acts as a fluid loss control agent and a viscosity reducing agent for the treatment fluids. As used herein, the term "compliant" refers to materials described in the US Code of Federal Regulations: 21 CFR §§ 170-199 (substances approved as food items, approved for contact for food, or approved for use as an additive to food) and that are prepared from food-grade materials. More particularly, as used herein, the term "compliant" refers to materials described in 21 CFR §§ 170-199 as at 5 March 2010.

[0031] Of the many advantages of the compositions and related methods of the present invention, is that treatment fluids of the present invention may improve oil and/or gas production by using dual-functional additives and reducing the number of additives required in a treatment fluid. The dual-functional additives suitable for use in the present invention provide

both fluid loss control and the ability to break the viscosity of the treatment fluid in which they are used over time. The self-degrading fluid loss control properties and the delayed-release breaking properties may lead to better conductivity in the treated portion of the subterranean formation. In certain embodiments, these dual-functional additives may reduce or eliminate the need for separate, multiple additives to provide fluid loss control and viscosity break. Moreover, the dual-functional additives suitable for use in the present invention have self-degrading properties whereby they may form a self-degrading filter cake that both reduces fluid loss and eliminates the need for a secondary solution to dissolve the filter cake after the subterranean operation is complete. In fact, in certain embodiments, the compliant dual-functional additives of the present invention may potentially eliminate the need for costly procedures needed to dispose of the treatment fluids containing non-compliant additives and may help reduce negative impacts on the marine environment and groundwater. Additionally, compliant dual-functional additives according to the present invention may provide effective treatment of the formation without excessive damage caused by the use of multiple or non-compliant additives.

[0032] In accordance with embodiments of the present invention, the treatment fluids generally comprise an aqueous base fluid, a viscosifying agent, and a compliant dual-functional additive that acts as both a fluid loss control agent and a viscosity reducing agent for the treatment fluids.

[0033] By way of example, the aqueous base fluid of embodiments of the treatment fluids of the present invention may be any fluid comprising an aqueous component. Suitable aqueous components include, but not limited to, fresh water, salt water, brine (*e.g.*, saturated or unsaturated saltwater), seawater, pond water and any combination thereof. Generally, the aqueous component may be from any source. Suitable aqueous base fluids may include foams. In certain embodiments, the viscosifying agents of the present invention may be difficult to dissolve in brines. To solve this problem, in one embodiment of the present invention, the viscosifying agent may be hydrated in fresh water prior to addition of the salt solution. One of ordinary skill in the art, with the benefit of the present disclosure, will recognize suitable aqueous base fluids for use in the treatment fluids and methods of the present invention. In some embodiments, the aqueous base fluid may be present in a treatment fluid of the present invention in an amount in the range of about 75% to about 99.9% of the treatment fluid. In some embodiments, fresh water may be the preferred aqueous base fluid.

[0034] The viscosifying agent of the present invention may be any suitable viscosifying agent that may perform the desired function. Suitable viscosifying agents may comprise any substance (*e.g.* a polymeric material) capable of increasing the viscosity of the treatment fluids. In certain embodiments, the viscosifying agent may comprise one or more polymers that have at least two molecules that are capable of forming a crosslink in a crosslinking reaction in the presence of a crosslinking agent, and/or polymers that have at least two molecules that are crosslinked (*i.e.*, a crosslinked viscosifying agent). The viscosifying agents may be biopolymers, polysaccharides, and/or derivatives thereof that contain one or more of these monosaccharide units: galactose, mannose, glucose, xylose, arabinose, fructose, glucuronic acid, or pyranosyl sulfate. The term "derivative" includes any compound that is made from one of the listed compounds, for example, by replacing one atom in the listed compound with another atom or group of atoms, rearranging two or more atoms in the listed compound, ionizing one of the listed compounds, or creating a salt of one of the listed compounds. Examples of suitable viscosifying agents include, but are not limited to, cellulose derivatives, carboxymethylguars, carboxymethylhydroxyethylguars, carboxymethylhydroxypropylguars, hydroxyethylcelluloses, carboxyethylcelluloses, carboxymethylcelluloses, carboxymethylhydroxyethylcelluloses, diutan gums, xanthan gums, galactomannans, hydroxyethylguars, hydroxypropylguars, scleroglucans, wellans, starches (also known as polysaccharide gums), and any derivative and combination thereof. In some embodiments a compliant viscosifying agent may be used, examples of suitable compliant viscosifying agents include carboxyethylcellulose, carboxymethylcellulose (CMC), carboxymethylhydroxyethylcellulose, and combination thereof.

[0035] The viscosifying agent may be present in the treatment fluids useful in the methods of the present invention in an amount sufficient to provide the desired viscosity. In some embodiments, the viscosifying agents may be present in an amount in the range of from about 0.01% to about 10% by weight of the treatment fluid. In other embodiments, the viscosifying agents may be cellulose derivatives present in an amount in the range of from about 0.1% to about 1% by weight of the treatment fluid. In other embodiments, the viscosifying agents may be starches present in the range of from about 3% to 5% by weight of the treatment fluid. In other embodiments, the viscosifying agents may be polysaccharides present from about 0.1% to 3% by weight of the treatment fluid. In some embodiments the viscosifying agent may be a mixture of a polysaccharide and a starch (as used herein, the term "starch" refers to a polysaccharide gum).

[0036] The compliant dual-functional additives suitable for use in the present invention may comprise any substance initially capable of preventing fluid loss of the treatment fluids by obstructing pore throats in the subterranean formation and subsequently capable of decreasing the viscosity of the treatment fluids through a double reaction mechanism. In certain embodiments, the dual-functional agent may comprise compounds that include any compliant ester capable of preventing fluid loss and breaking the viscous fluid in a controlled manner after well treatment is completed. An ester compound is defined as a compound that includes one or more carboxylate groups: R1--COO—R2, wherein R1 can be H and wherein R1 and R2 may be phenyl, methoxyphenyl, alkylphenyl, C1 -C11 alkyl, C1 -C.11 substituted alkyl, substituted phenyl, or other organic compound. Suitable esters include, but are not limited to, diesters, triesters, etc. Generally, suitable compliant dual-functional additives are immiscible in the treatment fluids and yet are capable of hydrolyzing over time in the presence of the water in the treatment fluid. Examples of suitable compliant esters include, but are not limited to, ethyl formate, propyl formate, butyl formate, amyl formate, anisyl formate, methyl acetate, propyl acetate, triacetin, butyl propionate, isoamyl propionate, ethyl lactate, methyl butyrate, ethyl isobutyrate, butyl isobutyrate, diethyl malonate, butyl ethyl malonate, dimethyl succinate, diethyl succinate, diethyl malate, diethyl tartrate, dimethyl tartrate, triethyl citrate, and any derivative and combination thereof. Suitable esters may include either substituted or unsubstituted alkyl groups.

[0037] In certain embodiments, a suitable dual-functional additive is an ester compound that degrades to form an acid thereby allowing the acid to act as a viscosity reducing agent for the treatment fluid. Suitable acids for use in the present invention include any compliant acid into which the compliant esters may degrade. Examples of such acids include, but are not limited to, formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, malonic acid, succinic acid, malic acid, tartaric acid, citric acid, and any combination thereof.

[0038] Without being limited by theory, it is believed that in certain embodiments the dual-functional additives provide fluid-loss control until the esters degrade into water-soluble components that subsequently break the viscosity of the treatment fluids through a double reaction mechanism, which may include both a hydrolysis reaction and a chelation reaction. By way of example, the dual-functional additive may catalyze hydrolysis of portions of the polymer backbone, and chelate crosslinking metal species that may be present; thereby reducing the viscosity. The combination of a degradable fluid-loss control agent and a delayed breaker may result in very low permeability damage and high conductivity once the reaction is complete. In

certain embodiments, the hydrolysis of the compliant dual-functional additives is dependent on the pH range of the treatment fluid and the solubility of the ester. In certain embodiments, the alkyl group of the ester that comes from the corresponding alcohol may control the solubility properties of the ester. By way of example, one skilled in the art will recognize that esters made from low carbon number alcohols, such as methanol and ethanol, generally have relatively higher water solubility. Thus, application temperature range for these esters may be lower than higher carbon atom esters. For higher temperature applications, esters formed from higher carbon number alcohols, such as *n*-propanol, butanol, hexanol, and cyclohexanol, may be more suitable. In other embodiments, esters formed from polycarboxylic acids may be well suited for use in high temperature applications. In certain embodiments, mixed esters with both high and low carbon numbers, may be used for high temperature applications (for example, 275°F (135°C) or above when using triethyl citrate) to achieve a more rapid viscosity break in the treatment fluids. Mixed esters may also be beneficial for moderate temperature applications (for example, 275°F (135°C) or below when using triethyl citrate). For example, combining a formate ester with triethyl citrate will increase the rate of hydrolysis of the triethyl citrate in a pH range from about 3.5 to about 5. In those embodiments, combining both formate and acetate esters may lead to a faster break in the viscosity of the treatment fluid. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate ester or combination of esters to include in a treatment fluid of the present invention based on, among other things, the temperature conditions of a particular application, the type of viscosifying agents used, the molecular weight of the viscosifying agents, the desired degree of viscosification, and the pH of the treatment fluid.

[0039] A compliant dual-functional additive may be present in the treatment fluids useful in the methods of the present invention in an amount sufficient to provide the desired effect. That is, sufficient to provide at least a portion of the desired fluid loss control and breaker action. In some embodiments, the dual-functional additives may be present in an amount in the range of from about 0.03% to about 3% by weight of the treatment fluid. In other embodiment, the dual-functional additives may be present in an amount in the range of from about 0.1% to about 1% by weight of the treatment fluid.

[0040] In certain embodiments, the treatment fluids of the present invention may be a foamed fluid (*e.g.*, a liquid that comprises a gas such as nitrogen, carbon dioxide, air, or methane). As used herein, the term "foamed" also refers to fluids such as commingled fluids. In some embodiments, a foamed treatment fluid may be desirable to, among other things, reduce

the amount of fluid that is required in a water sensitive subterranean formation, to reduce fluid loss in the formation, and/or to provide enhanced proppant suspension. In examples of such embodiments, the gas may be present in the range of from about 5% to about 98% by volume of the treatment fluid, and more preferably in the range of from about 20% to about 80% by volume of the treatment fluid. The amount of gas to incorporate in the fluid may be affected by many factors including the viscosity of the fluid and the wellhead pressures involved in a particular application. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the how much gas, if any, to incorporate into the treatment fluids of the present invention.

[0041] Depending on the use of the treatment fluid, in some embodiments, other additives may optionally be included in the treatment fluids of the present invention. Examples of such additives may include, but are not limited to, salts, pH control additives, surfactants, additional breakers, biocides, crosslinkers, additional fluid loss control agents, stabilizers, chelating agents, scale inhibitors, gases, mutual solvents, particulates, corrosion inhibitors, oxidizers, reducers, and any combination thereof. A person of ordinary skill in the art, with the benefit of this disclosure, will recognize when such optional additives should be included in a treatment fluid used in the present invention, as well as the appropriate amounts of those additives to include.

[0042] In those embodiments of the present invention where it is desirable to crosslink the viscosifying agent, the treatment fluid may comprise one or more crosslinking agents. The crosslinking agents may comprise a metal ion or similar component that is capable of crosslinking at least two molecules of the viscosifying agent. Examples of suitable crosslinking agents include, but are not limited to, magnesium ions, zirconium ions, titanium ions, aluminum ions, antimony ions, chromium ions, iron ions, copper ions, magnesium ions, and zinc ions. These ions may be provided by providing any compound that is capable of producing one or more of these ions as is well understood by those of skill in the art. Examples of such compounds include, but are not limited to, ferric chloride, magnesium oxide, zirconium lactate, zirconium triethanolamine, zirconium lactate triethanolamine, zirconium carbonate, zirconium acetylacetonate, zirconium malate, zirconium citrate, zirconium diisopropylamine lactate, zirconium glycolate, zirconium acetate lactate, zirconium triethanolamine glycolate, zirconium lactate glycolate, zirconium triisopropanolamine lactate, titanium lactate, titanium malate, titanium citrate, titanium ammonium lactate, titanium triethanolamine, and titanium acetylacetonate, aluminum lactate, aluminum citrate, aluminum acetate, antimony compounds,

chromium(III) compounds, iron(II) compounds, iron(III) compounds, copper compounds, zinc compounds, and combinations thereof. In certain embodiments of the present invention, the crosslinking agent may be formulated to remain inactive until it is "activated" by, among other things, certain conditions in the fluid (*e.g.*, pH, temperature, etc.) and/or interaction with some other substance.

[0043] In some preferred embodiments, a compliant crosslinking agent may be used. Examples of suitable compliant crosslinking metal ions (that is, ions capable of crosslinking) include, but are not limited to, zirconium compounds contained within 21 CFR §§ 170-199, aluminum compounds contained within 21 CFR §§ 170-199, titanium compounds contained within 21 CFR §§ 170-199, chromium(III) compounds contained within 21 CFR §§ 170-199, iron(II) compounds contained within 21 CFR §§ 170-199, iron(III) compounds contained within 21 CFR §§ 170-199, copper compounds contained within 21 CFR §§ 170-199, zinc compounds contained within 21 CFR §§ 170-199, and combinations thereof. Examples of such suitable compliant ion-containing compounds include but are not limited to ammonium zirconium carbonate, zirconium citrate, zirconium lactate citrate, zirconium oxide, titanium dioxide, aluminum nicotinate, aluminum sulfate, aluminum sodium sulfate, aluminum ammonium sulfate, chromium caseinate, chromium potassium sulfate, zinc sulfate, zinc hydrosulfite, magnesium chloride, magnesium sulfate, magnesium gulconate, copper sulfate, and copper gluconate.

[0044] When included, suitable crosslinking agents may be present in the treatment fluids useful in the methods of the present invention in an amount sufficient to provide a desired degree of crosslinking between molecules of the viscosifying agent. In certain embodiments, the crosslinking agent may be present in the treatment fluids of the present invention in an amount in the range of from about 0.005% to about 1% by weight of the treatment fluid. In other embodiments, the crosslinking agent may be present in the treatment fluids of the present invention in an amount in the range of from about 0.05% to about 0.1% by weight of the first treatment fluid and/or second treatment fluid. While crosslinking agents may be added in a concentrated solution, the numerical ranges given above refer to the percentage of metal ions by weight of the treatment fluid. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of crosslinking agent to include in a treatment fluid of the present invention based on, among other things, the temperature conditions of a particular application, the type of viscosifying agents used, the molecular weight of the viscosifying agents, the desired degree of viscosification, and/or the pH of the treatment fluid.

[0045] It generally takes greater horsepower to pump fluids that are more viscous; thus, it may be desirable to delay the crosslink of the treatment fluids of the present invention until the fluid is close to the area to be treated. Such delay allows the operator to pump a non-crosslinked (and thus less viscous) fluid over a longer distance before having to add horsepower to place the more viscous, crosslinked fluid. One skilled in the art will be familiar with known methods to delay crosslinking, such as encapsulation, chemical delays (*e.g.* chelating agents), etc. In some embodiments, the activation of the crosslinking agent may be delayed by encapsulation with a coating (*e.g.*, a porous coating through which the crosslinking agent may diffuse slowly or a degradable coating that degrades down hole) that delays the release of the crosslinking agent until a desired time or place. In other embodiments, chelating agents, such as lactic acid and oxalic acid, may be added to delay the crosslinking of the viscosifying agent.

[0046] The treatment fluids of the present invention may comprise particulates, such as proppant particulates or gravel particulates. Such particulates may be included in the treatment fluids of the present invention, for example, when a gravel pack is to be formed in at least a portion of the well bore, or a proppant pack is to be formed in one or more fractures in the subterranean formation. Particulates suitable for use in the present invention may comprise any material suitable for use in subterranean operations. Suitable materials for these particulates may include, but are not limited to, sand, bauxite, ceramic materials, glass materials, polymer materials, polytetrafluoroethylene materials (commonly sold under the trade name TEFLON®), nut shell pieces, cured resinous particulates comprising nut shell pieces, seed shell pieces, cured resinous particulates comprising seed shell pieces, fruit pit pieces, cured resinous particulates comprising fruit pit pieces, wood, composite particulates, and combinations thereof. Suitable composite particulates may comprise a binder and a filler material wherein suitable filler materials include silica, alumina, fumed carbon, carbon black, graphite, mica, titanium dioxide, calcium silicate, kaolin, talc, zirconia, boron, fly ash, hollow glass microspheres, solid glass, and combinations thereof. The mean particulate size generally may range from about 2 mesh to about 400 mesh on the U.S. Sieve Series; however, in certain circumstances, other mean particulate sizes may be desired and will be entirely suitable for practice of the present invention. In particular embodiments, preferred mean particulate size distribution ranges are one or more of 6/12, 8/16, 12/20, 16/30, 20/40, 30/50, 40/60, 40/70, or 50/70 mesh. It should be understood that the term "particulate," as used in this disclosure, includes all known shapes of materials, including substantially spherical materials, fibrous materials, polygonal materials (such as cubic materials), and mixtures thereof. Moreover, fibrous materials, that may or may

not be used to bear the pressure of a closed fracture, may be included in certain embodiments of the present invention. In certain embodiments, the particulates included in the treatment fluids of the present invention may be coated with any suitable resin or tackifying agent known to those of ordinary skill in the art. In certain embodiments, the particulates may be present in the treatment fluids of the present invention in an amount in the range of from about 0.5 pounds per gallon ("ppg") to about 30 ppg (about 60 kg/m^3 to about 3,600 kg/m^3) by volume of the treatment fluid.

[0047] A biocide may be included to the treatment fluids of the present invention to reduce bioburden of the fluid so as to avoid introducing an undesirable level of bacteria into the subterranean formation. Suitable examples of biocides may include both oxidizing biocides and nonoxidizing biocides. Examples of oxidizing biocides include, but are not limited to, sodium hypochlorite, hypochlorous acid, chlorine, bromine, chlorine dioxide, and hydrogen peroxide. Examples of nonoxidizing biocides include, but are not limited to, aldehydes, quaternary amines, isothiazolines, carbamates, phosphonium quaternary compounds, and halogenated compounds. Factors that determine what biocide will be used in a particular application may include, but are not limited to, cost, performance, compatibility with other components of the treatment fluid, kill time, and environmental compatibility. One skilled in the art with the benefit of this disclosure will be able to choose a suitable biocide for a particular application.

[0048] In some embodiments, UV radiation may be used to reduce the bioburden of a fluid in place of chemical biocides or used in conjunction with chemical biocides. One method of using UV light to reduce bioburden suitable for use in the present invention involves adding a photoinitiator to the treatment fluid and then exposing the treatment fluid to a UV light source. Such photoinitiators may absorb the UV light and undergo a reaction to produce a reactive species of free radicals that may in turn trigger or catalyze desired chemical reactions. Suitable organic photoinitiators for use in the present invention may include, but are not limited to, acetophenone, propiophenone, benzophenone, xanthone, thioxanthone, fluorenone, benzaldehyde, anthraquinone, carbazole, thioindigoid dyes, phosphine oxides, ketones, benzoin ethers, benzyl ketals, alpha-dialkoxyacetophenones, alpha-hydroxyalkylphenones, alpha-aminoalkylphenones, and acylphosphine oxides; any combination or derivative thereof. Suitable inorganic photoinitiators for use in the present invention are substances that, when exposed to UV light, will generate free radicals that will interact with the microorganisms as well as other organics in a given treatment fluid. Some suitable inorganic photoinitiators include, but are not limited to, nanosized metal oxides (*e.g.*, those that have at least one

dimension that is 1 nm to 1000 nm in size) such as titanium dioxide, iron oxide, cobalt oxide, chromium oxide, magnesium oxide, aluminum oxide, copper oxide, zinc oxide, manganese oxide, and any combination or derivative thereof.

[0049] Salts may optionally be included in the treatment fluids of the present invention for many purposes, including, for reasons related to compatibility of the treatment fluid with the formation and formation fluids. To determine whether a salt may be beneficially used for compatibility purposes, a compatibility test may be performed to identify potential compatibility problems. From such tests, one of ordinary skill in the art with the benefit of this disclosure will be able to determine whether a salt should be included in a treatment fluid of the present invention. Suitable salts include, but are not limited to, calcium chloride, sodium chloride, magnesium chloride, potassium chloride, sodium bromide, potassium bromide, ammonium chloride, sodium formate, potassium formate, cesium formate, mixtures thereof, and the like. The amount of salt that should be added should be the amount necessary for formation compatibility, such as stability of clay minerals, taking into consideration the crystallization temperature of the brine, *e.g.*, the temperature at which the salt precipitates from the brine as the temperature drops.

[0050] Examples of suitable pH control additives that may optionally be included in the treatment fluids of the present invention are bases and/or acid compositions. A pH control additive may be necessary to maintain the pH of the treatment fluid at a desired level, *e.g.*, to improve the effectiveness of certain breakers and crosslinkers, etc. In some instances, it may be beneficial to maintain the pH at 3.5-5. One of ordinary skill in the art with the benefit of this disclosure will be able to recognize a suitable pH for a particular application.

[0051] In one embodiment, the pH control additive may be an acid composition. Examples of suitable acid compositions may comprise an acid, an acid generating compound, and combinations thereof. Any known acid may be suitable for use with the treatment fluids of the present invention. Examples of acids that may be suitable for use in the present invention include, but are not limited to organic acids (*e.g.*, formic acids, acetic acids, carbonic acids, citric acids, glycolic acids, lactic acids, ethylenediaminetetraacetic acid (EDTA), hydroxyethyl ethylenediamine triacetic acid (HEDTA), and the like), inorganic acids (*e.g.*, hydrochloric acid, hydrofluoric acid, phosphonic acid, *p*-toluenesulfonic acid, and the like), and combinations thereof.

[0052] Examples of acid generating compounds that may be suitable for use in the present invention include, but are not limited to, esters, aliphatic polyesters, ortho esters, which

may also be known as ortho ethers, poly(ortho esters), which may also be known as poly(ortho ethers), poly(lactides), poly(glycolides), poly(ε-caprolactones), poly(hydroxybutyrates), poly(anhydrides), or copolymers thereof. The term "copolymer" as used herein is not limited to the combination of two polymers, but includes any combination of polymers, *e.g.*, terpolymers and the like. Derivatives and combinations also may be suitable. Other suitable acid-generating compounds include: esters including, but not limited to, ethylene glycol monoformate, ethylene glycol diformate, diethylene glycol diformate, glyceryl monoformate, glyceryl diformate, glyceryl triformate, triethylene glycol diformate and formate esters of pentaerythritol.

[0053] The pH control additive also may comprise a base to elevate the pH of the treatment fluid. Generally, a base may be used to elevate the pH of the mixture. Any known base that is compatible with the viscosifying agents of the present invention can be used in the treatment fluids of the present invention. Examples of suitable bases include, but are not limited to, sodium hydroxide, potassium carbonate, potassium hydroxide, sodium carbonate, and sodium bicarbonate. One of ordinary skill in the art with the benefit of this disclosure will recognize the suitable bases that may be used to achieve a desired pH elevation.

[0054] In some embodiments, the treatment fluids of the present invention may include surfactants, *e.g.*, to improve the compatibility of the treatment fluids of the present invention with other fluids (like any formation fluids) that may be present in the well bore. One of ordinary skill in the art with the benefit of this disclosure will be able to identify the type of surfactant as well as the appropriate concentration of surfactant to be used. Suitable surfactants may be used in a liquid or powder form. Where used, the surfactants may be present in the treatment fluid in an amount sufficient to prevent incompatibility with formation fluids, other treatment fluids, or well bore fluids. In an embodiment where liquid surfactants are used, the surfactants are generally present in an amount in the range of from about 0.01% to about 5.0% by volume of the treatment fluid. In other embodiments, the liquid surfactants are present in an amount in the range of from about 0.1% to about 2.0% by volume of the treatment fluid. In embodiments where powdered surfactants are used, the surfactants may be present in an amount in the range of from about 0.001% to about 0.5% by weight of the treatment fluid.

[0055] In some embodiments, the surfactant may be a viscoelastic surfactant. These viscoelastic surfactants may be cationic, anionic, nonionic, amphoteric, or zwitterionic in nature. The viscoelastic surfactants may comprise any number of different compounds, including methyl ester sulfonates (*e.g.*, as described in U.S. Patent Application Nos. 2006/0180310, 2006/0180309, 2006/0183646 and U.S. Pat. No. 7,159,659, the relevant disclosures of which are

incorporated herein by reference), hydrolyzed keratin (*e.g.*, as described in U.S. Pat. No. 6,547,871, the relevant disclosure of which is incorporated herein by reference), sulfosuccinates, taurates, amine oxides, ethoxylated amides, alkoxylated fatty acids, alkoxylated alcohols (*e.g.*, lauryl alcohol ethoxylate, ethoxylated nonyl phenol), ethoxylated fatty amines, ethoxylated alkyl amines (*e.g.*, cocoalkylamine ethoxylate), betaines, modified betaines, alkylamidobetaines (*e.g.*, cocoamidopropyl betaine), quaternary ammonium compounds (*e.g.*, trimethyltallowammonium chloride, trimethylcocoammonium chloride), derivatives thereof, and combinations thereof. In certain embodiments, the surfactant may comprise a compliant surfactant such as sodium lauryl sulfate, polyoxyethylene (20) sorbitan monolaurate (commonly known as Polysorbate 20 or Tween 20), polysorbate 60 polysorbate 65, polysorbate 80, or sorbitan monostearate.

[0056] It should be noted that, in some embodiments, it may be beneficial to add a surfactant to a treatment fluid of the present invention as that fluid is being pumped downhole to help eliminate the possibility of foaming. However, in those embodiments where it is desirable to foam the treatment fluids of the present invention, surfactants such as HY-CLEAN (HC-2) surface-active suspending agent or AQF-2 additive, both commercially available from Halliburton Energy Services, Inc., of Duncan, Oklahoma, may be used. Additional examples of foaming agents that may be utilized to foam and stabilize the treatment fluids of this invention include, but are not limited to, betaines, amine oxides, methyl ester sulfonates, alkylamidobetaines such as cocoamidopropyl betaine, alpha-olefin sulfonate, trimethyltallowammonium chloride, C_8 to C_{22} alkylethoxylate sulfate and trimethylcocoammonium chloride. Other suitable foaming agents and foam stabilizing agents may be included as well, which will be known to those skilled in the art with the benefit of this disclosure.

[0057] In some embodiments of the present invention the treatment fluids may comprise breakers in addition to the dual functional additives described herein. Examples of such suitable breakers for treatment fluids of the present invention include, but are not limited to, sodium chlorites, hypochlorites, perborate, persulfates, peroxides, including organic peroxides. Other suitable breakers include, but are not limited to, suitable acids and peroxide breakers, delinkers, as well as enzymes that may be effective in breaking viscosified treatment fluids. In some preferred embodiments, the breaker may be a compliant breaker such as citric acid, other acids or chelating molecules found in 21 CFR §§ 170-199 (e.g.. tetrasodium EDTA 175.300), oxidizers found in 21 CFR §§ 170-199 (e.g. ammonium persulfate 175.150), enzymes found within 21 CFR §§ 170-199 (e.g. cellulose enzymes 173.120). A breaker may be included in a

treatment fluid of the present invention in an amount and form sufficient to achieve the desired viscosity reduction at a desired time. The breaker may be formulated to provide a delayed break, if desired. For example, a suitable breaker may be encapsulated if desired. Suitable encapsulation methods are known to those skilled in the art. One suitable encapsulation method involves coating the selected breaker in a porous material that allows for release of the breaker at a controlled rate. Another suitable encapsulation method that may be used involves coating the chosen breakers with a material that will degrade when downhole so as to release the breaker when desired. Resins that may be suitable include, but are not limited to, polymeric materials that will degrade when downhole.

[0058] A treatment fluid of the present invention may optionally comprise an activator or a retarder to, among other things, optimize the break rate provided by a breaker. Any known activator or retarder that is compatible with the particular breaker used is suitable for use in the present invention. Examples of such suitable activators include, but are not limited to, acid generating materials, chelated iron, copper, cobalt, and reducing sugars. Examples of suitable retarders include sodium thiosulfate, methanol, and diethylenetriamine. In some embodiments, the sodium thiosulfate may be used in a range of from about 1 to about 100 lb/Mgal (about 0.1 to about 12 kg/m^3) of treatment fluid. Note, as used herein, "pounds per thousand gallons" may be expressed as "lb/Mgal" or "pptg." A preferred range may be from about 5 to about 20 lb/Mgal (about 0.6 to about 2.4 kg/m^3). An artisan of ordinary skill with the benefit of this disclosure will be able to identify a suitable activator or retarder and the proper concentration of such activator or retarder for a given application.

[0059] In certain embodiments of the present invention, the breakers may be encapsulated by synthetic and natural waxes. Waxes having different melting points may be used in order to control the delay of breaking based on the temperature of a specific subterranean operation. In an embodiment, the encapsulation of the breaker is performed by mixing the breaker and wax above the melting temperature for the specific wax and then extruding the composition to form small particles of the encapsulated material. The resulting product may be annealed by briefly heating the product to the point of the coating to seal cracks in the coating, thus preventing premature release. The encapsulation may also be achieved by melt spraying the wax on the breaker (*e.g.* citric acid) particles or by any other technique known by a person of ordinary skill in the art. If used, a breaker should be included in a treatment fluid of the present invention in an amount sufficient to facilitate the desired reduction in viscosity in a treatment fluid. For instance, peroxide concentrations that may be used vary from about 0.1 to

about 30 gallons (about 0.4 to about 110 liters) of peroxide per 1000 gallons (about 3.8 m^3) of the treatment fluid. Similarly, for instance, when citric acid is used as a breaker, concentrations of from 0.1 lb/Mgal to 30 lb/Mgal (about 0.01 kg/m^3 to about 3.6 kg/m^3) are appropriate.

[0060] In other embodiments, it may be desirable to use a compliant dual-functional additive without using a substantial amount of another breaker. That is, to have at least about 75% to about 100% of the viscosity reduction be due to the use of the dual functional additive rather than to the use of an additional breaker.

[0061] In some embodiments of the present invention the treatment fluids may comprise additional fluid loss control additives known in the art in addition to the dual functional additives described herein. Examples of such additional fluid loss control agents include, but are not limited to, starches, silica flour, gas bubbles (energized fluid or foam), benzoic acid, soaps, resin particulates, relative permeability modifiers, and other immiscible fluids. It is also known in the art to use a dispersion of diesel in fluid as a fluid loss control agent; however, its use may have negative environmental impacts. If included, a fluid loss additive may be included in an amount of about 5 to about 2000 lb/Mgal of the treatment fluid. In some embodiments, the fluid loss additive may be included in an amount from about 10 to about 50 lb/Mgal of the treatment fluid. For some liquid additives that function as fluid loss additives, these may be included in an amount from about 0.01% to about 20% by volume; in some embodiments, these may be included in an amount from about 1.0% to about 10% by volume.

[0062] However, in other embodiments, it may be desirable to use a compliant dual-functional additive without using a substantial amount of another fluid loss control additive. That is, to have at least about 75% to about 100% of the fluid loss control be due to the use of the dual functional additive rather than to the use of an additional fluid loss control additive.

[0063] In other embodiments, it may be desirable to use a compliant dual-functional additive without using a substantial amount of another fluid loss control additive or a substantially amount of another breaker. That is, to have at least about 75% to about 100% of the fluid loss control and 75-100% of the viscosity reduction be due to the use of the dual functional additive rather than to the use of an additional fluid loss control additive or breaker.

[0064] The methods and treatment fluids of the present invention may be used during or in preparation for any subterranean operation wherein a fluid may be used. Suitable subterranean operations may include, but. are not limited. to, drilling operations, drill-in operations, fracturing operations, sand control treatments (*e.g.*, gravel packing), acidizing treatments (*e.g.*, matrix acidizing, fracture acidizing, removal of filter cakes and fluid loss pills),

"frac-pack" treatments, well bore clean-out treatments, and other suitable operations where a treatment fluid of the present invention may be useful. One of ordinary skill in the art, with the benefit of the present disclosure, will recognize suitable operations in which the treatment fluids of the present invention may be used.

[0065] When selected dual-functional additive is in a liquid form, it is preferably dispersed into the aqueous base fluid such that it forms "particles" or "beads" of dual-functional additive within the continuous phase of the aqueous base fluid . It is within the ability of one skilled in the art to disperse a selected dual-functional additive liquid into the aqueous base fluid.

[0066] In certain embodiments, the present invention provides methods that include a method comprising: providing a fracturing fluid comprising an aqueous base fluid, a viscosifying agent, and a compliant dual-functional additive; and introducing the fracturing fluid into at least a portion of a subterranean formation at a rate and pressure sufficient to create or enhance at least one or more fractures in the subterranean formation. In these embodiments, a treatment fluid of the present invention may be pumped into a well bore that penetrates a subterranean formation at a sufficient hydraulic pressure to create or enhance one or more cracks, or "fractures," in the subterranean formation. "Enhancing" one or more fractures in a subterranean formation, as that term is used herein, is defined to include the extension or enlargement of one or more natural or previously created fractures in the subterranean formation. The treatment fluids of the present invention used in these embodiments optionally may comprise particulates, often referred to as "proppant particulates," that may be deposited in the fractures. The proppant particulates may function to prevent one or more of the fractures from fully closing upon the release of hydraulic pressure, forming conductive channels through which fluids may flow to the well bore. Once at least one fracture is created and the proppant particulates are substantially in place, the viscosity of the treatment fluid of the present invention may be reduced (*e.g.*, through the use of a gel breaker, or allowed to reduce naturally over time) to allow it to be recovered.

[0067] In certain embodiments, the treatment fluids of the present invention may be used in acidizing and/or acid fracturing operations. In these embodiments, a portion of the subterranean formation is contacted with a treatment fluid of the present invention comprising one or more organic acids (or salts thereof) and one or more inorganic acids that interact with subterranean formation to form "voids" (*e.g.*, cracks, fractures, wormholes, etc.) in the formation. After acidization is completed, the treatment fluid of the present invention (or some

portion thereof) may be recovered to the surface. The remaining voids in the subterranean formation may enhance the formation's permeability, and/or increase the rate at which fluids subsequently may be produced from the formation. In certain embodiments, a treatment fluid of the present invention may be introduced into the subterranean formation at or above a pressure sufficient to create or enhance one or more fractures within the subterranean formation. In other embodiments, a treatment fluid of the present invention may be introduced into the subterranean formation below a pressure sufficient to create or enhance one or more fractures within the subterranean formation.

[0068] In certain embodiments, the present invention provides methods that include a method comprising: providing a treatment fluid comprising an aqueous base fluid, a viscosifying agent, and a compliant dual-functional additive; introducing the treatment fluid into at least a portion of the subterranean formation and allowing the dual-functional additive to minimize fluid loss by obstructing pore throats within the subterranean formation.

[0069] In certain embodiments, the present invention provides methods that include a method comprising: providing a treatment fluid comprising an aqueous base fluid, a viscosifying agent, and a compliant dual-functional additive; introducing the treatment fluid into at least a portion of the subterranean formation and allowing the formation of a filter cake in the range of less than about 1mm. The filter cake formed by the treatment fluids of the present invention may be a "self-degrading" filter cake. As referred to herein, the term "self-degrading filter cake" will be understood to mean a filter cake that may be removed without the need to circulate a separate a clean-up solution. Though the filter cakes formed by the treatment fluids of the present invention constitute self-degrading filter cakes, an operator may choose to circulate a separate clean up solution through the well bore under certain circumstances, such as when the operator desires to hasten the rate of degradation of the filter cake.

[0070] To facilitate a better understanding of the present invention, the following examples of the preferred embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

EXAMPLES

[0071] The following examples are submitted for the purpose of demonstrating the performance characteristics of the treatment fluids of the present invention.

EXAMPLE 1

[0072] Initially the viscosity of a treatment fluid that did not contain a dual functional additive (such as either a triethyl citrate (TEC), ethyl formate (EF), amyl formate (AF), triacetin (TA), or diethyl malonate (DEM)) was obtained to provide a reference point for comparison. The samples were prepared by dissolving 1.080 g of Cekol 30000 in 150 g of tap water with shear in a small, glass blender jar. After hydrating for a minimum of 30 minutes, the esters were added at the concentrations as noted, followed by 1.4 ml (0.93% v/v) of aluminum crosslinker. All gels were strongly crosslinked upon addition of the crosslinker. Table 1 lists the prepared sample treatment fluids and their pH values.

TABLE 1

Prepared Sample Treatment Fluids and pH Values

Ester	Fluid initial pH
none	4.57
5 gal/Mgal TEC	4.18
50 gal/Mgal TEC	3.80
50 gal/Mgal TEC + 10 gal/Mgal EF	3.79
5 gal/Mgal TEC + 10 gal/Mgal EF	4.37

[0073] Next, the viscosity of the treatment fluid above further containing 5 gal/Mgal of TEC and 50 gal/Mgal of TEC and, optionally, 10 gal/Mgal of EF were also measured. Viscosity was measured on a Chandler model 5550 fitted with a B5X bob and R1 rotor. A constant shear rate of 40 sec^{-1} was used in all tests. The test temperature was 180 °F (82°C). The maximum heating rate was used to heat the sample from ambient temperature to the test temperature. Figure 1 is a plot of viscosity curves as a function of time for the treatment fluids. Both the Figure 1 and the data show that a combination of TEC and EF lead to a more rapid breaking of the viscosity with lower concentrations of TEC. This should allow the treatment fluid to be more cost efficient and generate desired viscosity adequate for transport and placement during a subterranean operation.

EXAMPLE 2

[0074] Treatment fluids were prepared containing Aluminum-crosslinked 60 lb/Mgal CMC gel with one or more of the following dual-functional additives: TEC, amyl formate (AF), triacetin (TA), or diethyl malonate (DEM). For each fluid, the esters were present in the treatment fluid in the form of small droplets. Testing to determine final viscosity and pH was performed and the results show that each of the tested dual-functional additives (esters) used with this invention were capable of reducing the viscosity of the treatment fluid. As can be seen in Table 1, advantageous results were found using a combination of TEC and AF. In addition, TA also improved the viscosity break. DEM was sufficient to break the gel upon release of malonic acid. The results are shown in Table 2. The sample treatment fluids were prepared with the same polymer and crosslinker concentration as in example 1. All of the fluids initially were crosslinked gels. For the static break test procedure, the samples were placed in 8 oz Falcon cups, capped, and set in a water bath at the indicated test temperature for the specified time. After breaking, the viscosity was measured on a Haake RS150 fitted with a Z40 Couette system at a shear rate of 40 sec^{-1} and a temperature of 25 °C.

TABLE 2

Static Break Values for CMC gel containing TEC, AF, TA, and DEM

Breaker	Temperature (°F/°C)	Time (hr)	Final Viscosity (@ 40 sec^{-1})	Final pH
10 gal/Mgal AF	180/82	18	140	3.40
20 gal/Mgal AF	180/82	18	36	3.21
5 gal/Mgal TEC	180/82	18	420	4.28
5 gal/Mgal TEC, 10 gal/Mgal AF	180/82	18	62	3.45
5 gal/Mgal TEC, 20 gal/Mgal AF	180/82	18	18	3.17
5 gal/Mgal TEC, 10 gal/Mgal TA	180/82	24	21	3.32
5 gal/Mgal TEC, 10 gal/Mgal TA	180/82	23	25	3.87
5 gal/Mgal TEC,	180/82	23	25	3.80

20 gal/Mgal TA				
20gal/Mgal DEM	180/82	21	6	-

EXAMPLE 3

[0075] Treatment fluids containing 60 lb/Mgal Al-crosslinked CMC with and without TEC were prepared. In addition, treatment fluids containing 40 lb/Mgal Hybor G (a borate crosslinked guar available from Halliburton Energy Services, Inc. of Duncan, Oklahoma) were used as a comparison. The fluid loss properties of the treatment fluids were tested. Figure 2 is a plot of dynamic fluid loss curves as a function of time for the treatment fluids and it shows that fluid loss was about half of that observed by the 40 lb/Mgal Hybor G treatment fluid. Thus, the dual functional additives of the present invention are capable of acting a fluid loss control agents.

[0076] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope of the present invention. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the specified range is also suitable for use in the present invention and is hereby specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in

this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

1. A method comprising: providing a treatment fluid comprising an aqueous base fluid, a viscosifying agent, and a compliant dual-functional additive; and introducing the treatment fluid into at least a portion of the subterranean formation.

2. A method according to claim 1, wherein the compliant dual-functional additive restricts the flow of a fluid through pore throats within the subterranean formation.

3. A method according to claim 1 or 2, wherein the compliant dual-functional additive comprises an ester selected from the group consisting of: ethyl formate, propyl formate, butyl formate, amyl formate, anisyl formate, methyl acetate, propyl acetate, triacetin, butyl propionate, isoamyl propionate, ethyl lactate, methyl butyrate, ethyl isobutyrate, butyl isobutyrate, diethyl malonate, butyl ethyl malonate, dimethyl succinate, diethyl succinate, diethyl malate, diethyl tartrate, dimethyl tartrate, triethyl citrate, and any combination thereof.

4. A method according to claim 1, 2 or 3, wherein the compliant dual-functional additive degrades to form an acid, and the acid acts as a viscosity reducing agent for the treatment fluid.

5. A method according to claim 4, wherein the acid is selected from the group consisting of: formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, malonic acid, succinic acid, malic acid, tartaric acid, citric acid, and any combination thereof.

6. A method according to any preceding claim, wherein the viscosifying agent is selected from the group consisting of: a carboxymethylguar, a carboxymethylhydroxyethylguar, a carboxymethylhydroxypropylguar, a hydroxyethyl cellulose, a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, diutan gum, a xanthan gum, a galactomannan, a cellulose derivative, a hydroxyethylguar, a hydroxypropylguar, a scleroglucan, a wellan, a starch, an acrylamide, an acrylate and any derivative and combination thereof.

7. A method according to claim any preceding, wherein the viscosifying agent is crosslinked.

8. A method according to any preceding claim, wherein a self-degrading filter cake is formed.

9. A method comprising: providing a fracturing fluid comprising an aqueous base fluid, a viscosifying agent, and a compliant dual-functional additive that acts as a fluid loss control agent and a breaker; and introducing the fracturing fluid into at least a portion of a subterranean formation at a rate and pressure sufficient to create or enhance at least one or more fractures in the subterranean formation.

10. A method according to claim 9, wherein the compliant dual-functional additive comprises an ester selected from the group consisting of: ethyl formate, propyl formate, butyl formate, amyl formate, anisyl formate, methyl acetate, propyl acetate, triacetin, butyl propionate, isoamyl propionate, ethyl lactate, methyl butyrate, ethyl isobutyrate, butyl isobutyrate, diethyl malonate, butyl ethyl malonate, dimethyl succinate, diethyl succinate, diethyl malate, diethyl tartrate, dimethyl tartrate, triethyl citrate, and any combination thereof.

11. A method according to claim 9 or 10, wherein the compliant dual-functional additive degrades to form an acid, and the acid acts as a viscosity reducing agent for the fracturing fluid.

12. A method according to claim 11 wherein the acid is selected from the group consisting of: formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, malonic acid, succinic acid, malic acid, tartaric acid, citric acid, and any combination thereof.

13. A method according to claim 9 wherein the viscosifying agent is selected from the group consisting of: a carboxymethylguar, a carboxymethylhydroxyethylguar, a carboxymethylhydroxypropylguar, a hydroxyethylcellulose, a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, diutan gum, a xanthan gum, a galactomannan, a cellulose derivative, a hydroxyethylguar, a hydroxypropylguar, scleroglucan, a wellan, a starch, an acrylamide, an acrylate and any derivative and combination thereof.

14. A method according to claim 9, wherein the viscosifying agent is crosslinked.

15. A method according to any one of claims 1 to 8, wherein the compliant dual-functional additive comprises a fluid loss control agent and a breaker; and and the method comprises allowing the dual-functional additive to minimize fluid loss by obstructing at least one pore throat in the subterranean formation.

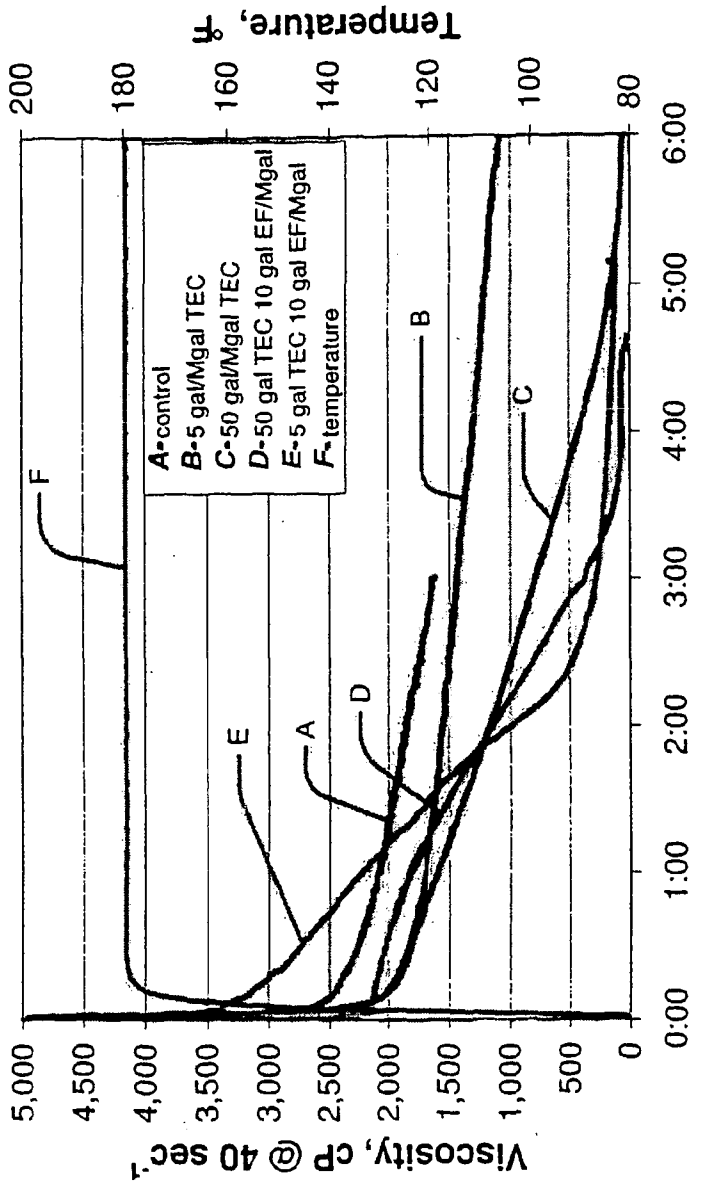

Viscosity, cP @ 40 sec-1
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
Temperature, °F
200
180
160
140
120
100
80
0:00
1:00
2:00
3:00
4:00
5:00
6:00
Time, hr:min
A-control
B-5 gal/Mgal TEC
C-50 gal/Mgal TEC
D-50 gal TEC 10 gal EF/Mgal
E-5 gal TEC 10 gal EF/Mgal
F-temperature
A
B
C
D
E
F

FIG. 1

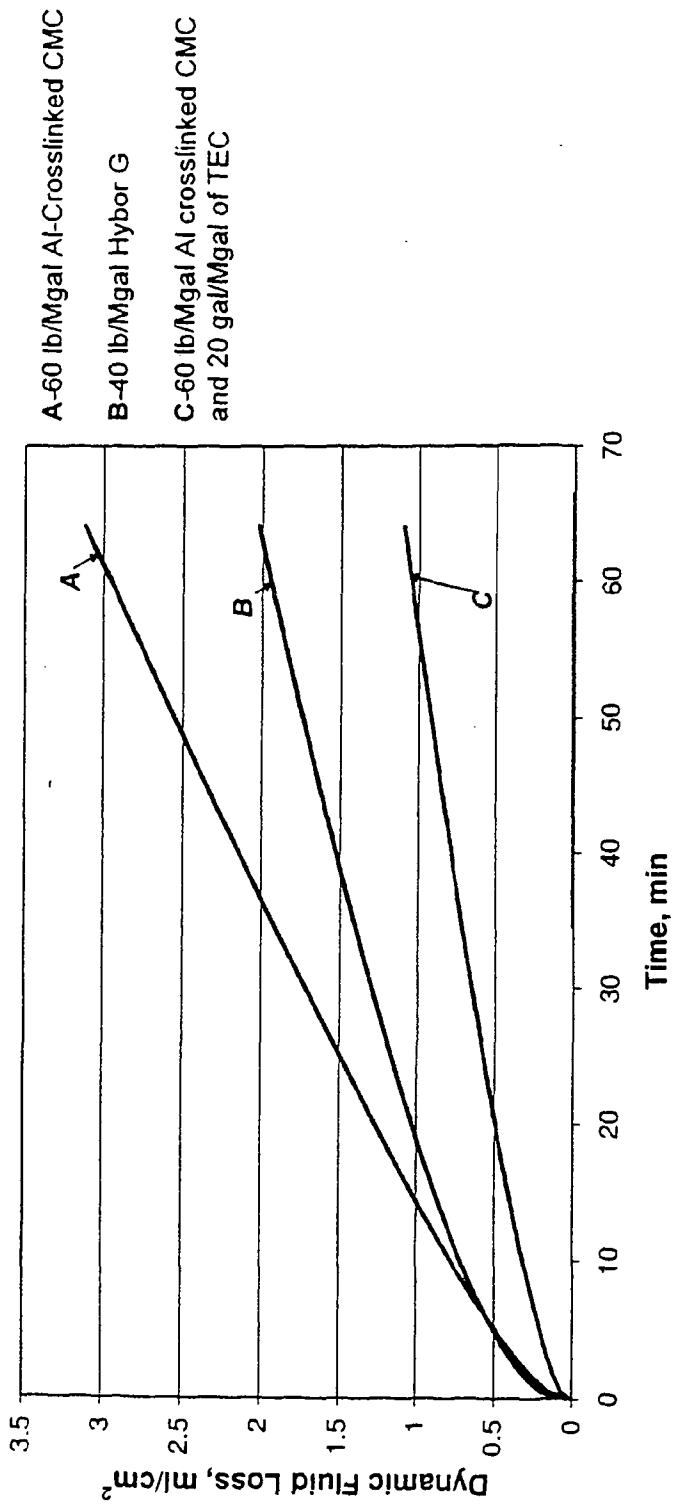

A-60 lb/Mgal Al-Crosslinked CMC
B-40 lb/Mgal Hybor G
C-60 lb/Mgal Al crosslinked CMC and 20 gal/Mgal of TEC
A
B
C
Dynamic Fluid Loss, ml/cm²
Time, min
0
0.5
1
1.5
2
2.5
3
3.5
0
10
20
30
40
50
60
70

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/000317

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/512 C09K8/68
ADD.

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 2008/119374 A1 (WILLBERG DEAN M [US] ET AL) 22 May 2008 (2008-05-22) paragraphs [0039], [0 66], [0 67], [102] the whole document	1-15
X	US 2006/116296 A1 (KIPPIE DAVID P [US] ET AL) 1 June 2006 (2006-06-01) paragraphs [0081] - [0101] the whole document	1-15
X	US 2007/078063 A1 (MUNOZ TRINIDAD JR [US]) 5 April 2007 (2007-04-05) paragraph [0030]; claims 1-7 the whole document	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 June 2011	10/06/2011

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/000317

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/036088 A1 (TODD BRADLEY L [US]) 28 March 2002 (2002-03-28) paragraphs [0027], [0029], [0039]; claims 1,9,10,11 the whole document -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2011/000317

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US 2002036088 A1	28-03-2002	NONE	