(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 September 2011 (09.09.2011)

PCT

(10) International Publication Number
WO 2011/107759 A1

(51) International Patent Classification:
C09K 8/10 (2006.01) *C09K 8/68* (2006.01)

(21) International Application Number:
PCT/GB2011/000318

(22) International Filing Date:
7 March 2011 (07.03.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/718,382 5 March 2010 (05.03.2010) US

(71) Applicant *(for all designated States except US)*: **HALLIBURTON ENERGY SERVICES INC.** [US/US]; PO Box 1431, Duncan, OK 73536 (US).

(71) Applicant *(for MW only)*: **CURTIS, Philip Anthony** [GB/GB]; A. A. Thornton & Co, 235 High Holborn, London WC1V 7LE (GB).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **LOVELESS, David M.** [US/US]; 1539 N. 13th Street, Duncan, OK 73533 (US). **HARRIS, Phillip C.** [US/US]; 2002 Woodrock Drive, Duncan, OK 73533 (US). **SAINI, Rajesh K.** [IN/US]; 421 South 27th Street, Apt. #K, Duncan, OK 73533 (US). **TONMUKAYAKUL, Narongsak** [TH/US]; 1704 Wilshire Drive, Duncan, OK 73533 (US). **LIANG, Feng** [CN/US]; 2402 Meadowview Drive, Duncan, OK 73533 (US).

(74) Agents: **COTTRILL, Emily Elizabeth Helen** et al.; A. A. Thornton & Co, 235 High Holborn, London WC1V 7LE (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

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

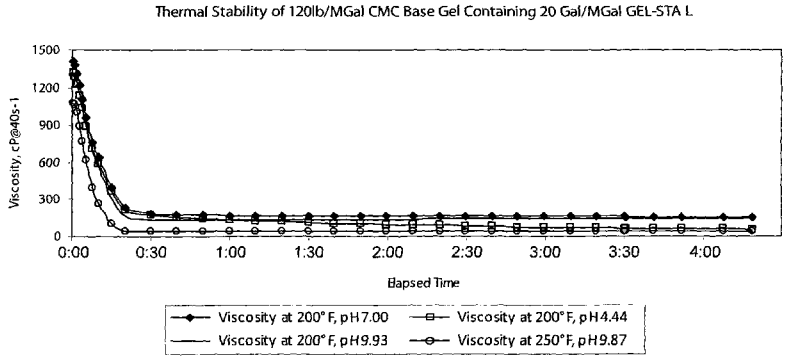


FIG. 1

(57) **Abstract**: Treatment fluids comprising an aqueous base fluid, a compliant cellulosic viscosifying agent, a crosslinking agent, and a protective ligand 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 compliant cellulosic viscosifying agent, a crosslinking agent, and a protective ligand 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.

WO 2011/107759 A1

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 cellulosic viscosifying agent having at least one ligand complex crosslink, and methods of use employing such treatment fluids to treat subterranean formations.

[0002] Viscosified treatment fluids have been used in a variety of subterranean treatments. 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. In well completion and stimulation operations, viscosified treatment fluids are often used to carry particulates into a subterranean formation for various purposes, *e.g.*, to deliver particulates to a desired location within a well bore. Examples of subterranean operations that use viscosified treatment fluids include servicing and completion operations such as fracturing, gravel packing, frac-packing, acidizing, acid fracturing, and fluid-loss pill formation.

[0003] In fracturing for example, fractures may be created or enhanced by introducing a viscosified fracturing fluid into the formation at a rate sufficient to exert a sufficient pressure on the formation to create and extend fractures therein. Generally, the viscosified fracturing fluid is introduced into the hydrocarbon producing zone within a subterranean formation. 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 sand control operations, for example, gravel packing operations, a screen, slotted liner, or other mechanical device is often placed into a portion of a well bore. A viscosified gravel pack fluid is used to deposit particulates, often referred to as a gravel, into the annulus between the mechanical device and the formation or casing to inhibit the flow of particulates from a portion of the subterranean formation to the well bore.

[0004] The viscosified treatment fluids used in subterranean operations are oftentimes aqueous-based fluids comprising viscosifying agents that increase the viscosities of the treatment fluids to, among other things, enhance the ability of the treatment fluids to suspend sand or other particulate materials. These viscosifying agents are typically polysaccharides which, when hydrated and at sufficient concentration, are capable of forming a viscous solution.

[0005] Numerous polysaccharides are used in the art to help viscosify a treatment fluid for use in subterranean operations. Some typical viscosifying agents include diutan gums, xanthan gums, galactomannans, and scleroglucans. However, the use of these conventional viscosifying agents may give rise to other problems. First, these viscosifying agents contain a considerable amount of insoluble residue that may lead to poor permeability and conductivity thereby leading to decreased hydrocarbon production. Furthermore, most fluid systems employing such polysaccharides also include a crosslinking agent such as metal ion crosslinkers. In some instances, the crosslinked viscosified treatment fluids, particularly non-reversible crosslinked fluids may be unstable at high temperatures and shear-sensitive. In particular, high temperature or shear may lead to loss of viscosity. It would also be desirable to generate treatment fluid that do not suffer shear degradation and thereby avoid the above limitations. In addition, fluid systems may be harmful to the environment and require special processing prior to disposal. Thus, it is desirable to use clean viscosifying agents for treatment fluids to produce low environmental impact treatment fluids.

SUMMARY OF THE INVENTION

[0006] The present invention relates to fluids useful for subterranean operations, and more particularly, to treatment fluids comprising a compliant cellulosic viscosifying agent having at least one ligand complex crosslink, 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 having a first viscosity comprising: an aqueous base fluid, a cellulosic viscosifying agent, a crosslinking agent, and a protective ligand; and placing the treatment fluid in a subterranean formation. Advantageously, the cellulosic viscosifying agent is a compliant cellulosic viscosifying agent.

[0008] In an embodiment, the treatment fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity prior to being placed in the subterranean formation.

[0009] In an embodiment, the treatment fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity after being placed in the subterranean formation.

[0010] In an embodiment, the compliant cellulosic viscosifying agent is a carboxylated viscosifying agent selected from the group consisting of a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, and any combination thereof.

[0011] In an embodiment, the crosslinking agent is a compound capable of supplying a metal ion selected from the group consisting of: a zirconium ion, an iron ion, a titanium ion, an aluminum ion, a chromium ion, an antimony ion, and any combination thereof.

[0012] In an embodiment, the crosslinking agent comprises a compound capable of supplying an aluminum ion and wherein treatment fluid has a pH in the range of from about 3.5 to about 5.

[0013] In an embodiment, the protective ligand is an acid 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, ethylenediaminetetraacetic acid, sulfuric acid and any combination thereof.

[0014] In an embodiment, the treatment fluid is placed in the subterranean formation as part of a subterranean operation selected from the group consisting of a drilling operation, a fracturing operation, a completion operation, and a workover operation.

[0015] In an embodiment, the subterranean formation comprises a bottom hole temperature of up to and including about 275°F (135 °C).

[0016] According to another aspect of the present invention, there is provided a method comprising: providing a fracturing fluid having a first viscosity comprising: an aqueous base fluid, a cellulosic viscosifying agent, a crosslinking agent, and a protective ligand; 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. Advantageously, the cellulosic viscosifying agent is a compliant cellulosic viscosifying agent.

[0017] In an embodiment, the fracturing fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity prior to being placed in the subterranean formation.

[0018] In an embodiment, the fracturing fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity after being placed in the subterranean formation.

[0019] In an embodiment, the compliant cellulosic viscosifying agent is a carboxylated viscosifying agent selected from the group consisting of a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, and any combination thereof.

[0020] In an embodiment, the crosslinking agent is a compound capable of supplying a metal ion selected from the group consisting of : a zirconium ion, an iron ion, a titanium ion, an aluminum ion, a chromium ion, an antimony ion, and any combination thereof.

[0021] In an embodiment, the protective ligand is an acid 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, sulfuric acid, ethylenediaminetetraacetic acid, and any combination thereof.

[0022] In an embodiment, the subterranean formation comprises a bottom hole temperature of up to and including about 275°F (135 °C).

[0023] According to another aspect of the present invention, there is provided a method comprising: providing a treatment fluid having a pH in the range of about 3.5 to about 5 and having a first viscosity comprising: an aqueous base fluid, a cellulosic, carboxylated viscosifying agent, an aluminum crosslinking agent, and a protective ligand and placing the treatment fluid in a subterranean formation.

[0024] In an embodiment, the compliant cellulosic viscosifying agent is a carboxylated viscosifying agent selected from the group consisting of a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, and any combination thereof.

[0025] In an embodiment, the crosslinking agent is a compound capable of supplying a metal ion selected from the group consisting of : a zirconium ion, an iron ion, a titanium ion, an aluminum ion, a chromium ion, an antimony ion, and any combination thereof.

[0026] In an embodiment, the protective ligand is an acid 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, sulfuric acid, ethylenediaminetetraacetic acid, and any combination thereof.

[0027] 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

[0028] 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.

[0029] Figure 1 shows the thermal stability of a CMC gel at different pH and temperatures.

[0030] Figures 2 and 3 show the thermal stability of various amounts of CMC crosslinked with various amounts of metal cation crosslinker.

[0031] Figure 4 shows the thermal stability of a cation crosslinked CMC gel after adding a gel stabilizer.

[0032] Figure 5 shows the thermal stability of a cation crosslinked CMC gel at adjusted pH with HCl or buffer solution.

[0033] Figure 6 shows the delayed crosslinking of a CMC gel with a cation crosslinker.

[0034] Figure 7 shows the breaking of the viscosified treatment fluids of the present invention with various oxidizers.

[0035] Figure 8 shows the dynamic behavior of the viscosified treatment fluids of the present invention at 120°C.

[0036] Figure 9 shows the evolution of the storage (G') and loss (G") moduli during the crosslinking at 25°C in terms of the frequency sweep.

[0037] Figure 10 shows the evolution of time-dependent storage (G') and loss (G") moduli during the crosslinking at 25°C obtained through the multiwave technique and compared to using a single frequency time sweep.

[0038] Figure 11 shows the proppant settling properties in the viscosified treatment fluids of the present invention.

[0039] Figure 12 depicts the proppant settling analysis under static settling conditions for the treatment fluids of the present invention.

[0040] Figure 13 shows the proppant settling properties for the treatment fluids of the present invention under imposed shear rate of $20s^{-1}$.

[0041] Figure 14 shows the settling analysis under imposed shear rate of $20s^{-1}$ for the treatment fluids of the present invention after aging the sample for 1 hour.

[0042] Figure 15 shows the settling analysis under imposed shear rate of $20s^{-1}$ for the treatment fluids of the present invention after aging the sample for 3 hours.

[0043] Figure 16 shows the viscosity profile of a CMC/Al crosslinked system at 200°F (93°C).

[0044] Figure 17 shows the viscosity profile of a CMC/Al crosslinked system at 180°F (82°C).

[0045] Figure 18 shows the shear stability profile of CMC/Al crosslinked system at 180°F (82°C).

DESCRIPTION OF PREFERRED EMBODIMENTS

[0046] The present invention relates to fluids useful for subterranean operations, and more particularly, to treatment fluids comprising a compliant cellulosic viscosifying agent having at least one ligand complex crosslink, and methods of use employing such treatment fluids to treat subterranean formations.

[0047] The treatment fluids of the present invention may comprise a compliant cellulosic viscosifying agent with a protective ligand. 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.

[0048] 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 a compliant cellulosic viscosifying agent having at least one ligand complex crosslink. The compliant cellulosic viscosifying agents of the invention, as defined above potentially eliminates the need for costly procedures needed to dispose of the treatment fluids containing non-compliant viscosifying agents and may help reduce negative impacts on the marine environment and groundwater. Additionally, the compliant viscosifying agent may provide effective treatment of the formation without excessive damage caused by the use of multiple or non-compliant viscosifiers. The compliant cellulosic viscosifying agent used in the present invention may result in treated portions of a subterranean formation that experience enhanced regain permeability and better conductivity due to the absence of insoluble residue. Moreover, treatment fluids of the present invention may be more shear-stable and may be more temperature stable may exhibit enhanced elastic properties, and may exhibit enhanced particulate carrying ability.

[0049] In accordance with embodiments of the present invention, the treatment fluids generally comprise an aqueous base fluid, a compliant cellulosic viscosifying agent, a crosslinking agent, and a protective ligand. Wherein at least a portion of the polymers of the

compliant cellulosic viscosifying agent are crosslinked with ligand complex crosslinks. As used herein, the term "ligand complex crosslink" refers to the crosslink between a crosslinking agent/protective ligand complex and two polymers of the compliant cellulosic viscosifying agent. In certain embodiments, the ligand complex crosslink may be formed prior to the treatment fluid being placed into the subterranean formation. In other embodiments, the ligand complex crosslink may be delayed such that it forms once the treatment fluid is placed in a subterranean formation.

[0050] 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 cellulosic 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. 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.

[0051] Compliant cellulosic viscosifying agents suitable for use in the present invention include any carboxylated, cellulosic viscosifying agent capable of increasing the viscosity of the treatment fluids and capable of forming a crosslink in the presence of a crosslinking agent. Examples of suitable compliant cellulosic viscosifying agents include, but are not limited to carboxyethylcellulose, carboxymethylcellulose (CMC), carboxymethylhydroxyethylcellulose, and any combination thereof. 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.

[0052] The compliant cellulosic 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 cellulosic viscosifying agents may be present in an amount in the range of from about 0.01% to about 15% by weight of the treatment fluid. In

some preferred embodiments, the cellulosic viscosifying agents may be present in an amount in the range of from about 0.1% to about 3% by weight of the treatment fluid.

[0053] 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. One skill in the art will recognize that selection of a particular crosslinking agent will be governed by several considerations such as the type and molecular weight of the viscosifying agent(s), the conditions (such as temperature and pH) in the subterranean formation being treated, the safety handling requirements, and the conditions (such as temperature and pH) of the treatment fluid.

[0054] The 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 0.001% 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 0.005% to about 0.1% by weight of the 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 viscosity, and/or the pH of the treatment fluid..

[0055] Suitable crosslinking agents 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 known in the art. 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.

[0056] In some preferred embodiments, a compliant crosslinking agent may be used. Examples of suitable compliant crosslinking metal ions (that is, metal 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.

[0057] In an embodiment of the present invention, a protective ligand may be added to the treatment fluids of the present invention. The protective ligand may comprise any substance capable of reacting with the metal ion crosslinking agent and forming reversible ligand complex crosslink between polymers of the compliant cellulosic viscosifying agent to form a crosslinked treatment fluid. In some embodiments, the protective ligand of the present invention may be capable of preventing the metal ion crosslinker from forming insoluble residue. In certain embodiments, a suitable protective ligand may be an acid that allows the pH of the treatment fluid to reduce to less than about 5. Shear resistance, temperature stability, and viscosity recovery rate may be significantly increased in crosslinked compliant cellulosic treatment fluids when the pH of the treatment fluid is in the range of from about 3.5 to about .5. Suitable protective ligands for use in the present invention 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, sulfuric acid, ethylenediaminetetraacetic, and any combination thereof. In certain embodiments, the protective ligand that may be used in the treatment fluids useful in the methods of the present invention may comprise any substance capable of degrading into an acid. In some embodiments, the acid may provide a protective effect on the metal ion crosslinking agent as well as lowering the pH of the treatment fluid. In certain embodiments, the protective ligand may comprise any ester capable of degrading into an acid. Suitable esters include, but are not limited to, diesters, triesters, etc. Examples of suitable 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. The protective ligand may be present in the treatment fluids useful in the methods of the present invention in an amount sufficient to provide the desired effect. In some embodiments, the protective ligand may be present in an amount in the range of from about 1:3 to about 1:10 ratio of crosslinking agent to protective ligand. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate protective ligand 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 viscosity, and/or the pH of the treatment fluid.

[0058] Without wishing to be limited by theory, it is believed that the protective ligand may function by acting as a competitive ligand for the metal center of the crosslinking agent thereby forming a reversible crosslink afforded by the chemically liable bond between the metal ion and the protective ligand. The treatment fluids of the present invention exhibit increased shear resistance, better proppant suspension properties, and high temperature stability. In particular, the treatment fluids of the present invention may be used in high temperature environments of up to 275°F (135°C) or more. The protective ligand may also act to both protect the aluminum from forming insoluble particles and to act as a competitive ligand once the gel is formed. These properties causing a reversible bond to be formed that gives rise to the elastically dominated gel properties and the ability to reheal, both of which are desirable properties in subterranean treatment fluids, such as fracturing fluids. As used herein, the term "reheal" refers to a fluid's ability to repair damage caused by shear forces, such as the shear forces due to the process of the fluid being placed down hole. In some preferred embodiments,

one compliant crosslinker may be a compound formed from the combination of aluminum sulfate and lactic acid.

[0059] 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 co-mingled fluids. In some embodiments, it may be desirable that the treatment fluid is foamed 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 90% 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.

[0060] 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, breakers, biocides, 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.

[0061] The treatment fluids of the present invention also may comprise breakers capable of reducing the viscosity of the treatment fluid at a desired time. 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 ore 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. The terms "degrade," "degradation," or "degradable" refer to both the two relatively extreme cases of degradation that the degradable material may undergo, i.e., heterogeneous (or bulk erosion) and homogeneous (or surface erosion), and any stage of degradation in between these two. This degradation can be a result of, among other things, a chemical or thermal reaction or a reaction induced by radiation.

[0062] 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 of peroxide (about 0.4 to about 110 liters) 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.

[0063] Other suitable breakers include compliant breakers such as 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.

[0064] Optionally, a treatment fluid of the present invention may comprise an activator or a retarder to, among other things, optimize the break rate provided by the 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 lbs/Mgal of treatment fluid. A preferred range may be from about 5 to about 20 lbs/Mgal. 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.

[0065] The treatment fluids of the present invention also may comprise suitable fluid loss control agents. Such fluid loss control agents may be particularly useful when a treatment fluid of the present invention is being used in a fracturing application or in a fluid used to seal a formation from invasion of fluid from the well bore. Any fluid loss control agent that is compatible with the treatment fluids of the present invention is suitable for use in the present invention. Examples include, but are not limited to, starches (as used herein, "starch" refers to a polysaccharide gum), silica flour, gas bubbles (energized fluid or foam), benzoic acid, soaps, resin particulates, relative permeability modifiers, degradable gel particulates, 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.

[0066] Alternatively, other materials that have better environmental impact such as esters (*e.g.*, triethyl citrate, ethyl formate, triethyl orthoformate, amyl formate, diethyl malate, etc.) can be used as fluid loss liquids. These materials generate acid upon hydrolysis that helps in breaking the gel. In some cases, like triethyl citrate, the material generates citric acid that chelates with crosslinking metal ion in the fluid and break the fluid by taking away the metal crosslinker. A variety of organic acids are available in the form of esters that are compliant. Most of these are described as Synthetic Flavoring Substances and Adjuvants (21 CFR § 172.515). Another example of a suitable fluid loss control additive is one that comprises a degradable material. If included, a fluid loss additive should be added to a treatment fluid of the present invention in an amount necessary to give the desired fluid loss control. In some embodiments, a fluid loss additive may be included in an amount of about 5 to about 2000 lbs/Mgal of the treatment fluid. In some embodiments, the fluid loss additive may be included

in an amount from about 10 to about 50 lbs/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. Suitable compliant fluid loss control additives include 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.

[0067] 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, 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, meta-silicate, 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.

[0068] A biocide may be included to the treatment fluids of the present invention to reduce bioburden of the fluid 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.

[0069] 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.

[0070] 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.

[0071] 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 to reduce corrosion on any metal present in the well bore or formation, 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.

[0072] 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.

[0073] 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 one embodiment, 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.

[0074] 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.

[0075] It should be noted that, in some embodiments, it might be beneficial to add a surfactant to a treatment fluid of the present invention as that fluid is being pumped down hole 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 used 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.

[0076] 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, 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.

[0077] In certain embodiments, the present invention provides methods that include a method comprising: providing a fracturing fluid comprising an aqueous base fluid, a compliant cellulosic viscosifying agent, a crosslinking agent, and a protective ligand; 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, among other things, 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.*, using a gel breaker, or allowed to reduce naturally over time) to allow it to be recovered.

[0078] 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 (or salts thereof),

which 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, among other things, 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.

[0079] 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

[0080] The following examples are submitted for the purpose of demonstrating the performance characteristics of the treatment fluids of the present invention.

Example 1

[0081] In these examples, the viscosity of a treatment fluid that did not contain a protective ligand was obtained to provide a reference point for comparison. The viscosity of treatment fluids containing 40 lb/Mgal, 60 lb/Mgal, and 120 lb/Mgal of carboxymethylcellulose (CMC) was measured. The treatment fluids containing 60 lb/Mgal of CMC were prepared by adding 720mg of sodium CMC to 100mL of DI water in a blender at low speed and left to hydrate for 30 minutes to form a hydrated base gel. The amount of CMC added varied according to the final concentration of CMC desired. To the hydrated base gel was added 2 grams of KCl either in solid form or by dissolving in a minimum amount of water. The base gel was mixed to distribute the salt uniformly thought the mixture. Then the gel stabilizer (GEL-STA) was added to the base gel followed by addition of an appropriate amount of breaker when desired. Samples were aged for 1 hr before any measurement was taken.

[0082] The viscosity of the samples was measured using a Chandler viscometer with a B5X Bob at shear rate of 40 sec^{-1}. A 44mL sample of gelled fluid was transferred to the viscometer cup at 75°F (24°C) and placed on the viscometer. The temperature was ramped to

180°F (82°C) in 20 minutes. For the test at 250°F (120°C), the temperature was ramped to 250°F (120°C) in 30 minutes and maintained for 3 hours. Figures 2 and 3 plot the viscosity curves as a function of time for the zirconium crosslinked CMC fluids at various temperatures between 180°F and 250°F (between 82°C and 120°C). The viscosity of each sample was measured at a constant shear rate. Both Figures 1 and 2 show that the treatment fluids of the present invention are stable at high temperatures. After an initial thinning of the crosslinked gel, the viscosity of the gel remained virtually steady for 3 hours at the lower temperatures and 1.5 hours at the higher temperatures.

[0083] To be useful for various oil field applications the CMC base gel must be stable to various conditions of temperature and pH encountered in the down hole conditions. Therefore 120lb /Mgal CMC base gel was prepared and tested at different pH and temperature ranges to establish the robustness of the polymer chain. The tests were run in Chandler viscometer as discussed above. The results are shown in Figure 1 and indicated that the base gel degraded gradually in acidic condition but found to be very stable in the neutral to basic conditions.

[0084] Figures 16 and 17 show the viscosity plots for treatment fluids having 60 lb/Mgal of CMC crosslinked with aluminum only or crosslinked with an crosslinking agent and a protective ligand complex comprising a 1:4 ratio of aluminum to lactic acid. The protective ligand provides increased stability for the treatment fluids, especially at temperatures above 200°F (93°C). Figure 18 shows the shear stability profile of CMC/Al crosslinked system at 180°F (82°C).

Example 2

[0085] It has been found during this study that a thickened solution of sodium CMC can be prepared by first hydrating the polymer in fresh water followed by the addition of the required amount of salt either as solid or in solution form. Once hydrated the addition of salt has minimal effect on the viscosity of the base gel as shown in Table 2. The viscosity of CMC in high concentration brines was high enough to be useful for a variety of oil field applications. When CMC was added directly to a brine solution it did not hydrate quickly and the final viscosity did not reach the level reached when the base gel was prepared by the method of described herein. This problem was even more severe for concentrated brines (10% NaCl) or for higher valent salts (e.g. $CaCl_2$). "ClayFix II" refers to a temporary clay-stabilization additive commercially available from Halliburton Energy Services, Inc. of Duncan Oklahoma.

Table 1. Rheology of 40 lb/Mgal CMC in water and salt solution

Base Fluid	Salt (g/100 mL water)	Fann 35 Dial reading @ rpm				
		600	300	200	100	6
Deionized Water	None	77.0	56.0	45.5	31.0	5.0
Tap water	None	65.0	45.5	36.0	24.0	4.0
Deionized Water	1g KCl	52.0	36.0	27.5	18.0	3.0
Deionized Water	2g KCl	50.0	34.0	26.5	17.5	2.5
Deionized Water	2g $CaCl_2$	48.0	33.0	26.0	17.0	2.5
Deionized Water	11.1 g NaCl	53.0	36.0	28.0	18.0	3.0
Deionized Water	0.2 g of ClayFix II	63.0	44.5	35.5	24.5	4.0
Deionized Water	API Standard Brine Solution (10 g NaCl & 1.1g $CaCl_2$)	51.5	35.0	27.0	17.5	2.5
Deionized Water	7.5g NaCl; 0.82g $CaCl_2$; 0.385g $MgCl_2$ $6H_2O$	52.0	35.5	27.5	18.0	3.0

Example 3

[0086] Some treatment fluids were crosslinked with 3 gal/Mgal of a crosslinker with and without 1:4 ratio of crosslinker (Al) :protective ligand (lactic acid). The CMC base gel prepared in brine solution was crosslinked with polyvalent metal ions of zirconium and aluminum. The zirconium-based crosslinker, such as CL-23 commercially available from Halliburton Energy Services, Inc. of Duncan, Oklahoma, gave the best result in term of viscosity and stability. CL-23 formed stable gels with CMC in the pH range of 4 to 8 and more specifically in the range of 5 to 6.5. It was critical to keep the pH in this narrow range for optimum crosslinked viscosity. The crosslinked gels obtained from CL-23 and CMC fluid were much more stable at high temperature (250°F (120°C)) if the fluid is aged at room temperature for 1 hr. This increased stability may be due to the additional crosslinking between zirconium and carboxyl groups present in the CMC based fluid. The crosslinked fluids were tested on a Chandler viscometer for the gel stability at various temperatures. After an initial thermal thinning of the crosslinked gel the viscosity of the gels remained virtually steady for more than 3 hours at temperature of 180°F (82°C) and 225°F (107°C). At 250°F (120°C), the crosslinked gel viscosity remained

higher than 500 cP at 40 sec^{-1} for only 1.5 hours. Addition of gel stabilizer such as GEL-STA commercially available from Halliburton Energy Services, Inc. of Duncan, Oklahoma or purging with nitrogen gas improved the thermal stability of the gel at high temperature as seen in Figure 4. This may be explained by the exclusion of oxygen from the base gel, which otherwise oxidizes the polymer. Thermal stability was also improved by aging the crosslinked gel overnight presumably by increasing the number of crosslinking sites. Best viscosity was obtained by using 60 lb/Mgal CMC gel in distilled water crosslinked with 3 gal/Mgal of CL-23 at pH 5.9 in 2% KCl.

Example 4

[0087] The control of pH played an important role in the crosslinking and stability of the CMC gel. The pH of the CMC gel was adjusted with either diluted HCl or an ammonium acetate buffer solution, such as BA-20 commercially available from Halliburton Energy Services, Inc. of Duncan, Oklahoma. If the amount of BA-20 added is greater than 2 gal/Mgal then the viscosity of the final gel is lower. This may be due to the competition for zirconium ions between carboxylic group present in CMC and the acetic acid present in the BA-20. However, when added in small amount (<1 gal/Mgal) BA-20 did not effect the final viscosity as shown in Figure 5. The sequence of gel preparation follows the following steps: First CMC was hydrated in Duncan tap water followed by addition of KCl, then CL-23 and finally pH was adjusted by addition of HCl or BA-20.

Example 5

[0088] The CMC base gel tends to crosslink immediately on addition of CL-23, as shown in previous figures. Figure 6 shows the delay in crosslinking caused by the addition of lactic acid. The lactic acid prevents the crosslinking at lower temperature and when temperature reaches 130°F the rate of crosslinking increases and leads to a sudden rise in the viscosity of the fluid. The delayed crosslinking can be tailored by controlling the amount of the delaying agent, in this case lactic acid, used in the system.

Example 6

[0089] The metal ion crosslinked CMC gels could be easily broken down by traditional oxidizer breakers such as persulfates and t-butylhydroperoxide (HT Breaker) to afford clear solution without any trace of insoluble materials. The results are shown in Figure 7. The absence of insoluble materials in the broken fluid was important because these insoluble materials can plug the formation and thereby reduce the permeability of the formation. Reduced permeability leads to impaired conductivity and reduced rate of oil production. The Optiflo III

and HT breaker, both commercially available from Halliburton Energy Services, Inc., of Duncan, Oklahoma, at temperature of 180-200°F delay the breaking of gel for about 2 hours before the viscosity of crosslinked fluid goes below 500cP.

Example 7

[0090] The conductivity of the treatment fluids was tested on samples containing 60 lb/Mgal CMC gel crosslinked with 3 gal/Mgal of CL-23. The gel also contained 2% KCl and the pH was adjusted to a narrow range of 5-6.5 with BA-20. Two set of tests were run by adding 4 gal/Mgal and 8 gal/Mgal of HT breaker commercially available from Halliburton Services, Inc. of Duncan, Oklahoma to the crosslinked fluid at 200°F. 2 lb/ft^2 of 30/50 mesh proppants (ECONOPROP available from CarboCeramics, Inc. of Irving, Texas) were used in the cell at 6000 and 8000 psi closure pressure for the test. The results are shown in Table 2, each of the tested fluids contained 60 lb/Mgal of a CMC viscosifying agent and 3 gal/Mgal of a zirconium crosslinker (CL-23, commercially available from Halliburton Energy Services, Inc. in Duncan, Oklahoma) in an Ohio Sandstone core.

Table 2. Conductivity test of CMC based crosslinked treatment fluids

Proppant	Breaker	Temp (°F/°C)	Stress (psi)	Baseline (mD-ft)	Conductivity (MD-ft)	Regain Permeability
2 lb/ft^2 30/50 EconoProp	4 gpt HT breaker	200/93	6000	2730	1147	42%
2 lb/ft^2 30/50 EconoProp	4 gpt HT breaker	200/93	8000	1810	687	38%
2 lb/ft^2 30/50 EconoProp	8 gpt HT breaker	200/93	6000	2730	1236	45%
2 lb/ft^2 30/50 EconoProp	8 gpt HT breaker	200/93	8000	1810	769	42%

Example 8

[0091] Dynamic moduli were measured as a function of frequency, and the behavior of the storage (G') and loss (G") moduli of the 40 lb/Mgal CMC gel crosslinked with 4 gal/Mgal of CL-23 tested at 120°C are shown in Figure 8. The experimental results show one distinct trend of the moduli with respect to the frequency region. Gel-like behavior was observed, where the G' is greater than the G" and both moduli exhibit their independency to frequency. Also, over the frequency range tested, G' displays a characteristic plateau G'_P region. The G'_P behavior is typical of a "strong gel" material that is observed when the characteristic relaxation time of the material is longer than the process time, that is, time per cycle of oscillation.

[0092] The isothermal cure of the crosslinking system was followed by a dynamic time sweep, where the moduli G' and G" were monitored as a function of cure time at constant frequency. The G' versus time curve was then fitted to an empirical kinetic model such that suggested by Hsich. The ultimate modulus reached on cure was obtained from this experiment. However, it was shown that a single time sweep at a constant frequency is not sufficient for accurate determination of the gel time. The gel point (GP) of a crosslinking polymer is an important parameter, both from scientific and technological standpoints. Therefore, the evolution of tanδ with cure time was measured at different frequencies. The various curves coincide at a single point, corresponding to the GP. The dynamic moduli were obtained at different frequencies as crosslinking progressed using multiple waveform rheology where a compound waveform was applied on the sample. From the results of the mulitwave experiment, the GP was detected by the criteria mentioned above. Simultaneously, data for G' and G" as a function of curing time was extracted, for use in an appropriate kinetic model. The objective of this work was to characterize the cure of CMC crosslinking by Zr at room temperature, and effects of elastic and viscous properties on proppant transport under static and dynamic (applied shear rate).

[0093] Rheological studies were conducted on an Anton-Parr controlled Strain/stress rheometer (MCR501) using 50mm with 2° cone angle. The time for loading the sample was kept to a minimum so as to reduce the lag time for crosslinking. The multiwave experiment was run with a fundamental frequency of 1 $rad.s^{-1}$ (ω_f) and the strains (γ_i) were kept at 0.1% at each harmonic. A total of six waveforms were added to create the composite strain input, with the frequency ranging from 0.1 to 40 $rad.s^{-1}$. The instrument software had the capability to automatically perform the Fourier transformation of the raw data.

[0094] The multiwave technique generated frequency sweeps from 0.1 to 10 rad.s^{-1}, as the sample cures. For isothermal cure at 25°C, the evolution of microstructure with time is shown in terms of the frequency sweep as shown in Figure 9. It was observed that the G' increases in magnitude and becomes increasingly independent of frequency as the crosslinking progresses. Correspondingly, the level of G" dropped steadily with cure time. These observations indicated that the sample develops a predominantly elastic character and simultaneously lost its viscous characteristics. Qualitatively, the above behavior of the storage and loss moduli with cure time (shown in Figure 10) was typical of many thermosetting systems. The validity of the data obtained was verified using the multiwave technique by comparing it with continuous time sweep conducted at the same temperature. A time sweep performed at 1 rad.s^{-1} frequency and 0.1% strain shows excellent overlap with data from the multiwave experiment, corresponding to the same frequency as shown in Figure 10. The experiment results reveal that the crosslinked CMC with Zr sample has predominantly elastic character over the entire curing time, and reaches reach its gel stage after 3 hour of curing process at 25°C.

Example 9

[0095] Suspending ability of the invented fluid under a given imposed shear condition was directly determined using the developed flow through device as described in Patent Application Publication No. 2010/0018294 and incorporated by reference herein. The settling profile was obtained from a standard CCD camera (resolution 1024 × 1000 pixels) captured at different time interval using a proprietary particle-interface software that operates on MATLAB® software and the *ImageJ* image processing package. The one dimension settling velocity fields (v_{yz}) of the settling interface was calculated by cross-correlating corresponding intensity region in two successive images to determine the settling interface between proppant and crosslinked fluid.

[0096] Figure 11 shows a typical proppant suspending characteristic of 40 lb/Mgal CMC gel crosslinked with 2 gal/Mgal of CL-23 tested under static, defined as zero-imposed shear rate, condition. The sample was aged for 1 hour prior to taking any of the measurements. Figure 12 shows the settling profile analysis of the system using the proprietary particle interface software. The result reveals that crosslinked fluid supported the proppant particle for over the tested period. Analysis of the relationship between settling interface with processing time revealed that the settling velocity of proppant equaled to 0 cm/min. This might implies that under static

settling conditions, the invented fluid achieved a perfect suspending characteristic. However, settling of proppant particles was observed under dynamic settling condition, defined as there is an imposed shear rate onto the material, as shown in Figures 14 and 15.

[0097] Figures 13 and 14 show typical settling characteristics of proppant in 40 lb/Mgal CMC gel crosslinked with 4 gal/Mgal of CL-23 under dynamic settling, defined as having a shear rate directly imposed on to the sample while measuring proppant-settling profile. In this experiment, the dynamic settling was performed with an imposed shear rate of 20 s^{-1} condition. The dynamic settling experiments were conducted at two different curing times, 1 hour and 3 hour of curing processes. This is to investigate effect of elastic and gel structure on proppant suspending ability. Dissimilarity in suspending ability of the CMC-Zr crosslinked sample were observed in Figures 14 and 15, indicating the significance of curing time on proppant support ability of the system. The proppant settled within 90 minutes of shearing process for the sample being cured for 1 hour and shown in Figure 14, while the sample developed a greater suspendability when it was aged for 3 hours prior to commence the settling experiment as shown in Figure 15. Qualitatively, the settling behavior as a function of curing time indicated the significance of the crosslinking behavior as a function of time on proppant support ability. As the cure time progressed, the material became more dominant in its elastic character and lost its viscous characteristics.

[0098] 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 range 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 having a first viscosity comprising: an aqueous base fluid, a compliant cellulosic viscosifying agent, a crosslinking agent, and a protective ligand; and placing the treatment fluid in a subterranean formation.

2. A method according to claim 1, wherein the treatment fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity prior to being placed in the subterranean formation.

3. A method according to claim 1, wherein the treatment fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity after being placed in the subterranean formation.

4. A method according to claim 1, 2 or 3, wherein the compliant cellulosic viscosifying agent is a carboxylated viscosifying agent selected from the group consisting of a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, and any combination thereof.

5. A method according to any one of claims 1 to 4, wherein the crosslinking agent is a compound capable of supplying a metal ion selected from the group consisting of: a zirconium ion, an iron ion, a titanium ion, an aluminum ion, a chromium ion, an antimony ion, and any combination thereof.

6. A method according to claim 5, wherein the crosslinking agent comprises a compound capable of supplying an aluminum ion and wherein treatment fluid has a pH in the range of from about 3.5 to about 5.

7. A method according to any preceding claim, wherein the protective ligand is an acid 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, ethylenediaminetetraacetic acid, sulfuric acid and any combination thereof.

8. A method according to any preceding claim, wherein the treatment fluid is placed in the subterranean formation as part of a subterranean operation selected from the group consisting of a drilling operation, a fracturing operation, a completion operation, and a workover operation.

9. A method according to any preceding claim, wherein the subterranean formation comprises a bottom hole temperature of up to and including about 275°F.

10. A method comprising: providing a fracturing fluid having a first viscosity comprising: an aqueous base fluid, a compliant cellulosic viscosifying agent, a crosslinking agent, and a protective ligand; 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.

11. A method according to claim 10, wherein the fracturing fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity prior to being placed in the subterranean formation.

12. A method according to claim 10, wherein the fracturing fluid forms a crosslinked gel having a second viscosity, the second viscosity being higher than the first viscosity after being placed in the subterranean formation.

13. A method according to claim 10, 11 or 12, wherein the compliant cellulosic viscosifying agent is a carboxylated viscosifying agent selected from the group consisting of a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, and any combination thereof.

14. A method according to any one of claims 10 to 13, wherein the crosslinking agent is a compound capable of supplying a metal ion selected from the group consisting of : a zirconium ion, an iron ion, a titanium ion, an aluminum ion, a chromium ion, an antimony ion, and any combination thereof.

15. A method according to any one of claims 10 to 14, wherein the protective ligand is an acid 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, sulfuric acid, ethylenediaminetetraacetic acid, and any combination thereof.

16. A method according to any one of claims 10 to 15, wherein the subterranean formation comprises a bottom hole temperature of up to and including about 275°F.

17. A method according to claim 1, wherein the treatment fluid has a pH in the range of about 3.5 to about 5, the compliant cellulosic viscosifying agent is a cellulosic, carboxylated viscosifying agent, and the crosslinking agent is an aluminum crosslinking agent.

18. A method according to claim 17, wherein the compliant cellulosic viscosifying agent is a carboxylated viscosifying agent selected from the group consisting of a carboxyethylcellulose, a carboxymethylcellulose, a carboxymethylhydroxyethylcellulose, and any combination thereof.

19. A method according to claim 17 or 18, wherein the crosslinking agent is a compound capable of supplying a metal ion selected from the group consisting of : a zirconium ion, an iron ion, a titanium ion, an aluminum ion, a chromium ion, an antimony ion, and any combination thereof.

20. A method according to claim 17, 18 or 19, wherein the protective ligand is an acid 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, sulfuric acid, ethylenediaminetetraacetic acid, and any combination thereof.

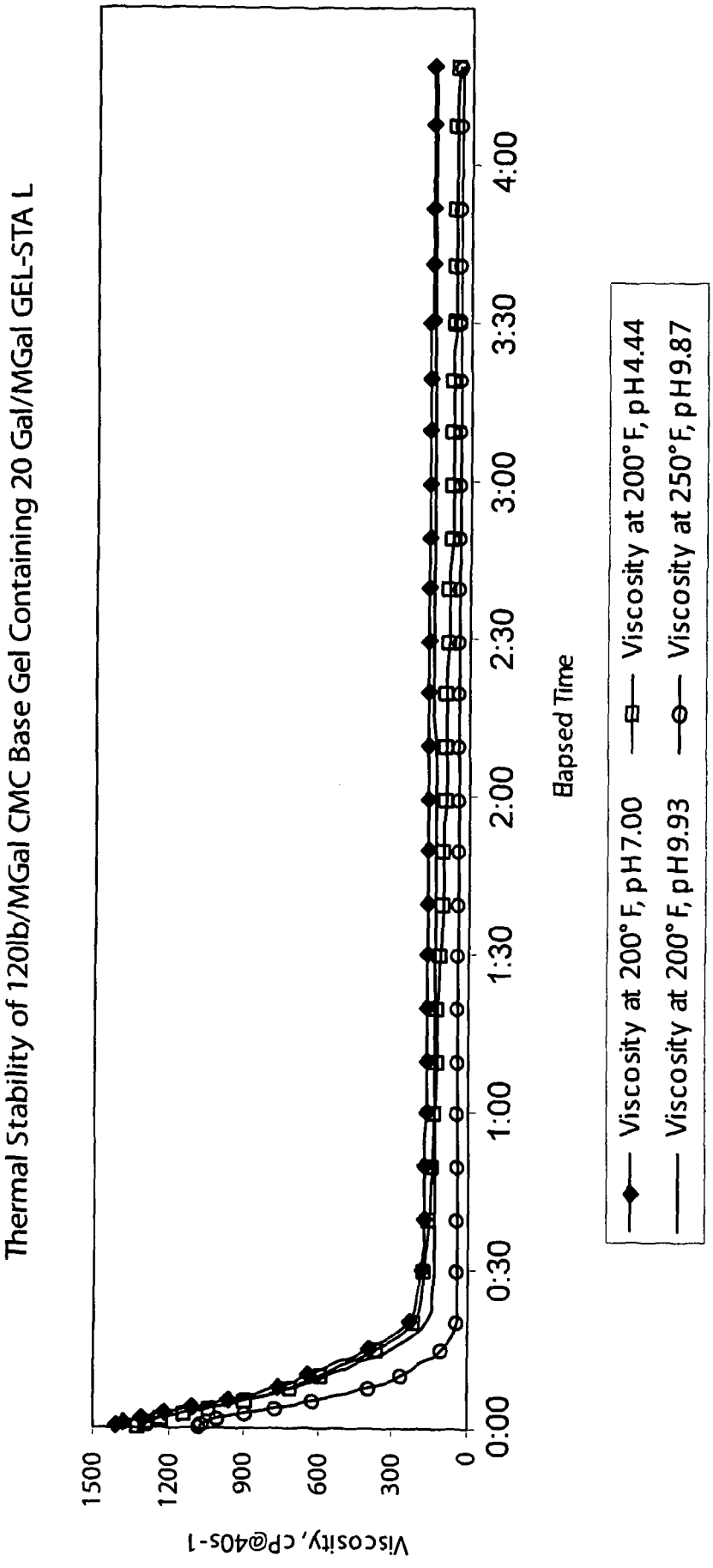

Thermal Stability of 120lb/MGal CMC Base Gel Containing 20 Gal/MGal GEL-STA L
Viscosity, cP@40s-1
1500
1200
900
600
300
0
0:00
0:30
1:00
1:30
2:00
2:30
3:00
3:30
4:00
Elapsed Time
Viscosity at 200°F, pH7.00
Viscosity at 200°F, pH9.93
Viscosity at 200°F, pH4.44
Viscosity at 250°F, pH9.87

FIG. 1

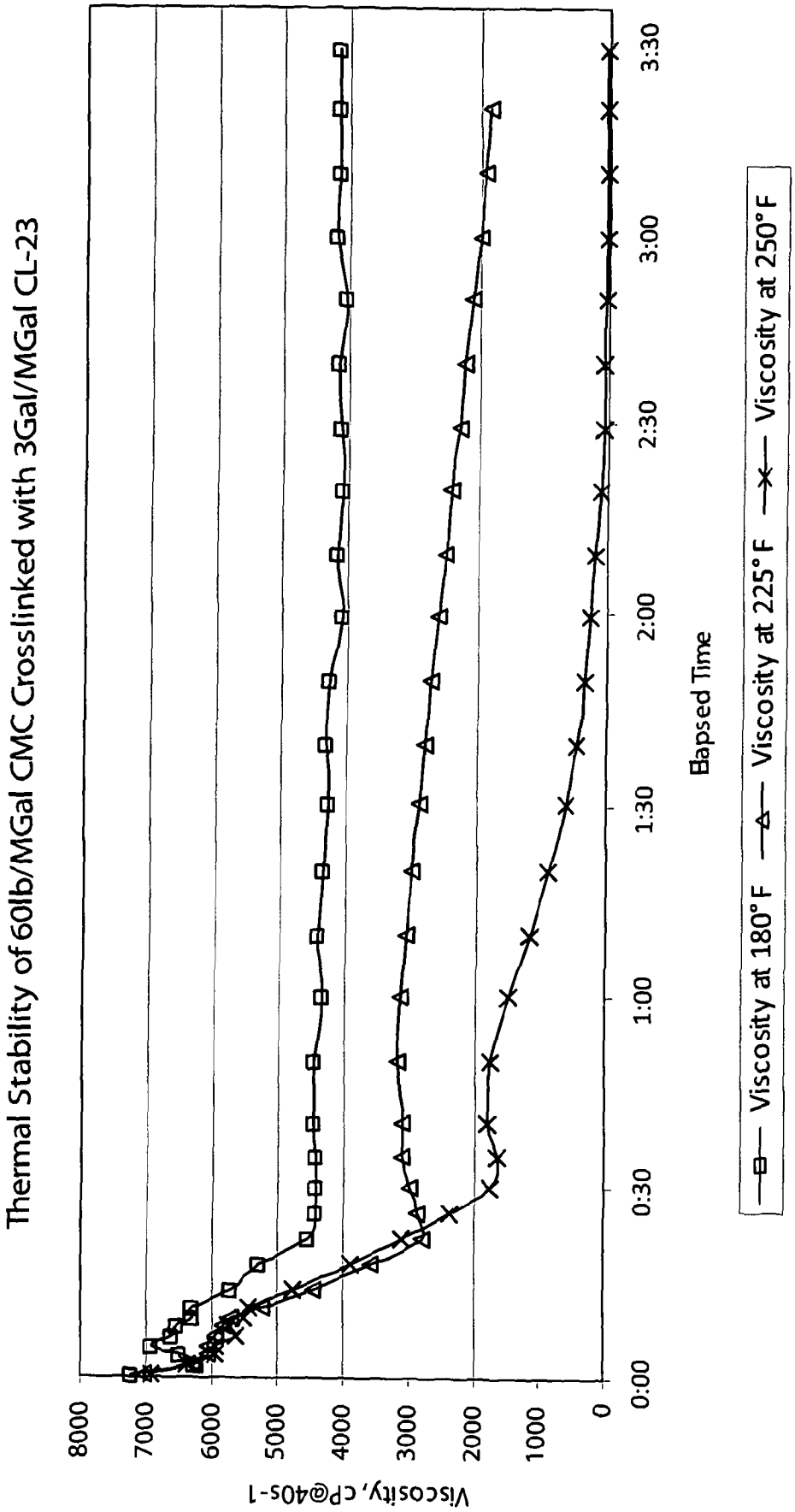

Thermal Stability of 60lb/MGal CMC Crosslinked with 3Gal/MGal CL-23
Viscosity, cP@40s-1
8000
7000
6000
5000
4000
3000
2000
1000
0
0:00
0:30
1:00
1:30
2:00
2:30
3:00
3:30
Elapsed Time
Viscosity at 180° F
Viscosity at 225° F
Viscosity at 250° F

FIG. 2

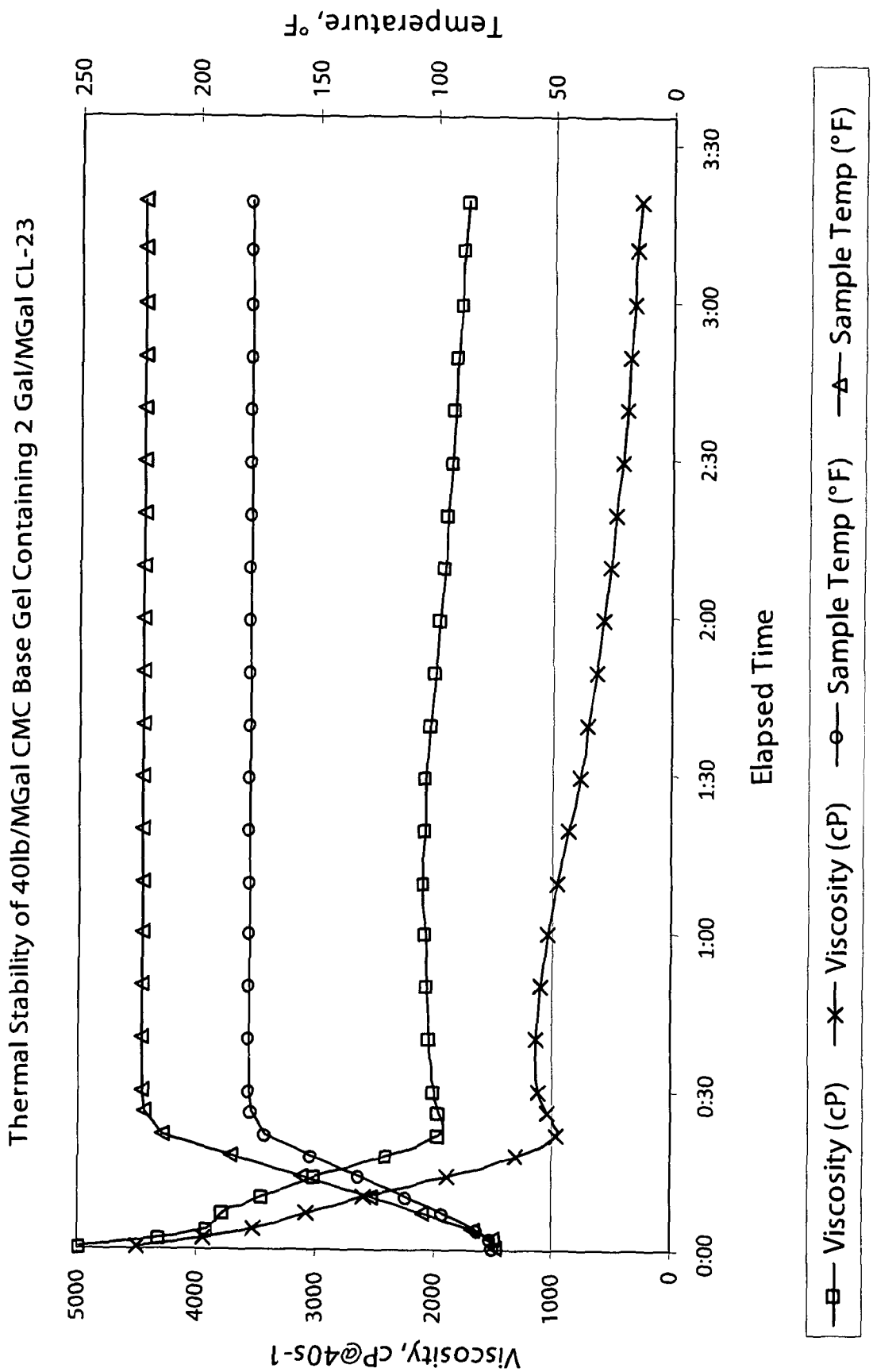

Thermal Stability of 40lb/MGal CMC Base Gel Containing 2 Gal/MGal CL-23
Viscosity, cP@40s-1
Temperature, °F
Elapsed Time
0:00
0:30
1:00
1:30
2:00
2:30
3:00
3:30
0
1000
2000
3000
4000
5000
0
50
100
150
200
250
Viscosity (cP)
Viscosity (cP)
Sample Temp (°F)
Sample Temp (°F)

FIG. 3

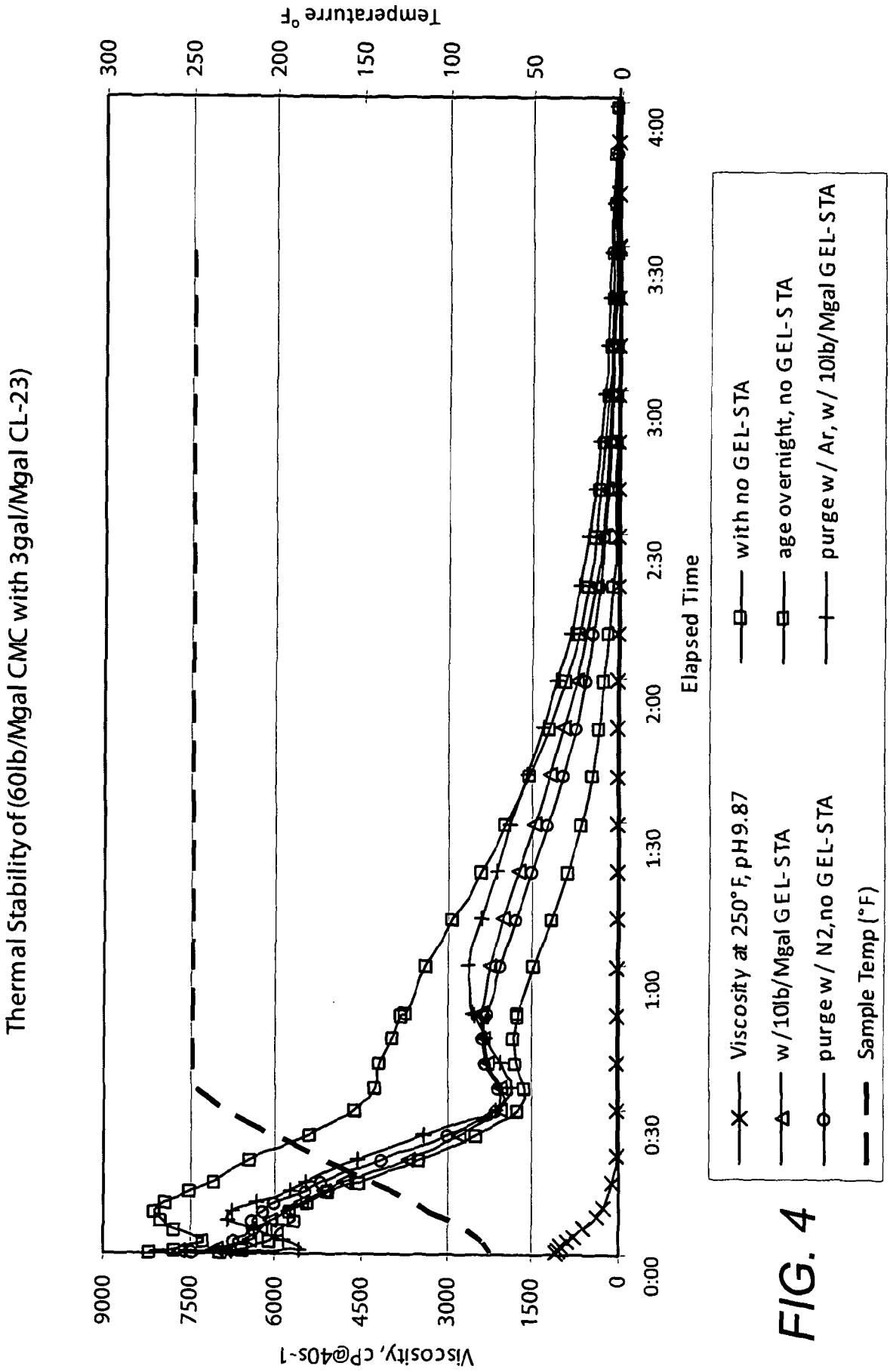

Thermal Stability of (60lb/Mgal CMC with 3gal/Mgal CL-23)
Viscosity, cP@40s-1
Temperature °F
Elapsed Time
0:00
0:30
1:00
1:30
2:00
2:30
3:00
3:30
4:00
0
1500
3000
4500
6000
7500
9000
0
50
100
150
200
250
300
Viscosity at 250°F, pH9.87
w/10lb/Mgal GEL-STA
purge w/ N2, no GEL-STA
Sample Temp (°F)
with no GEL-STA
age overnight, no GEL-STA
purge w/ Ar, w/ 10lb/Mgal GEL-STA

FIG. 4

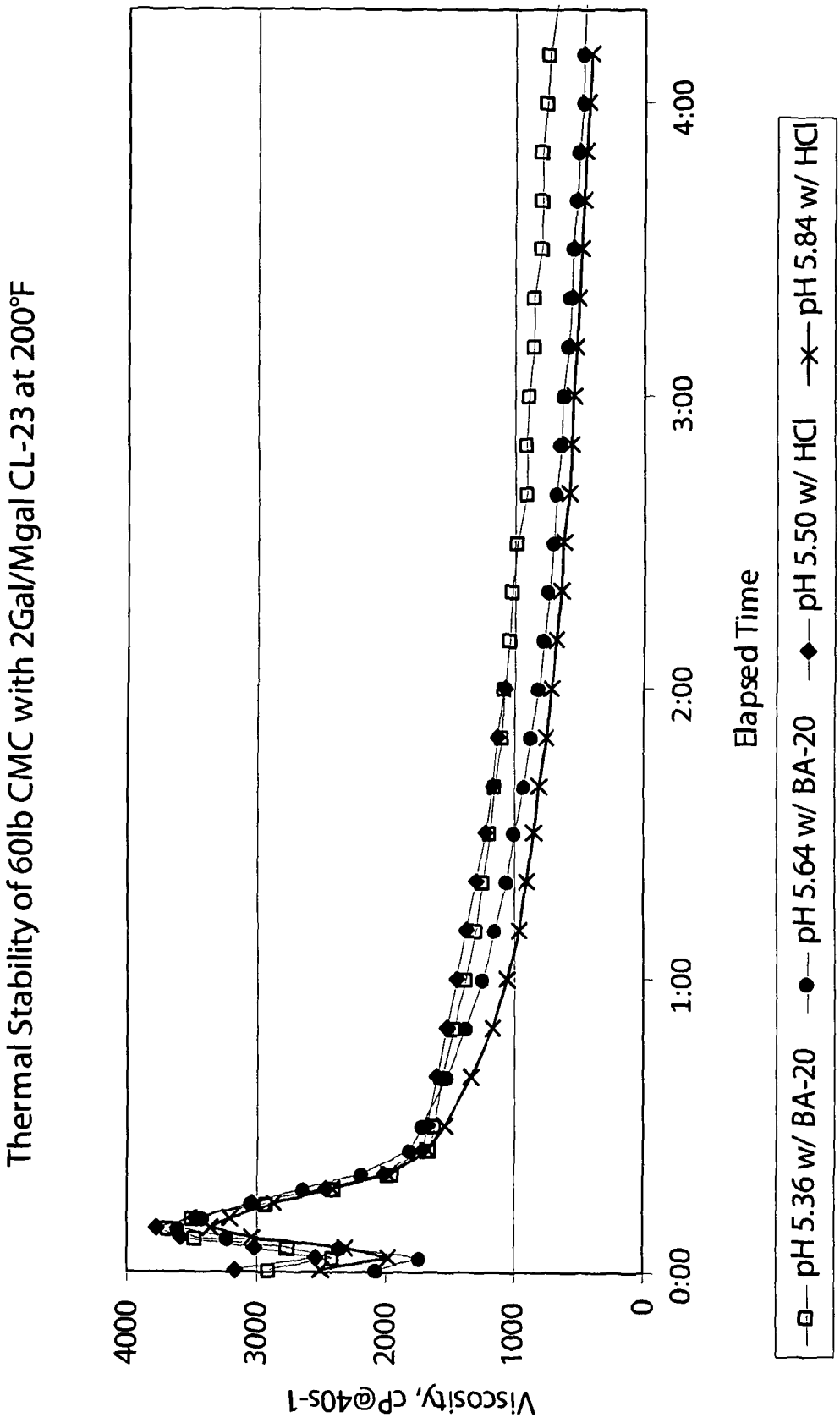

Thermal Stability of 60lb CMC with 2Gal/Mgal CL-23 at 200°F
Viscosity, cP@40s-1
4000
3000
2000
1000
0
0:00
1:00
2:00
3:00
4:00
Elapsed Time
pH 5.36 w/ BA-20
pH 5.64 w/ BA-20
pH 5.50 w/ HCl
pH 5.84 w/ HCl

FIG. 5

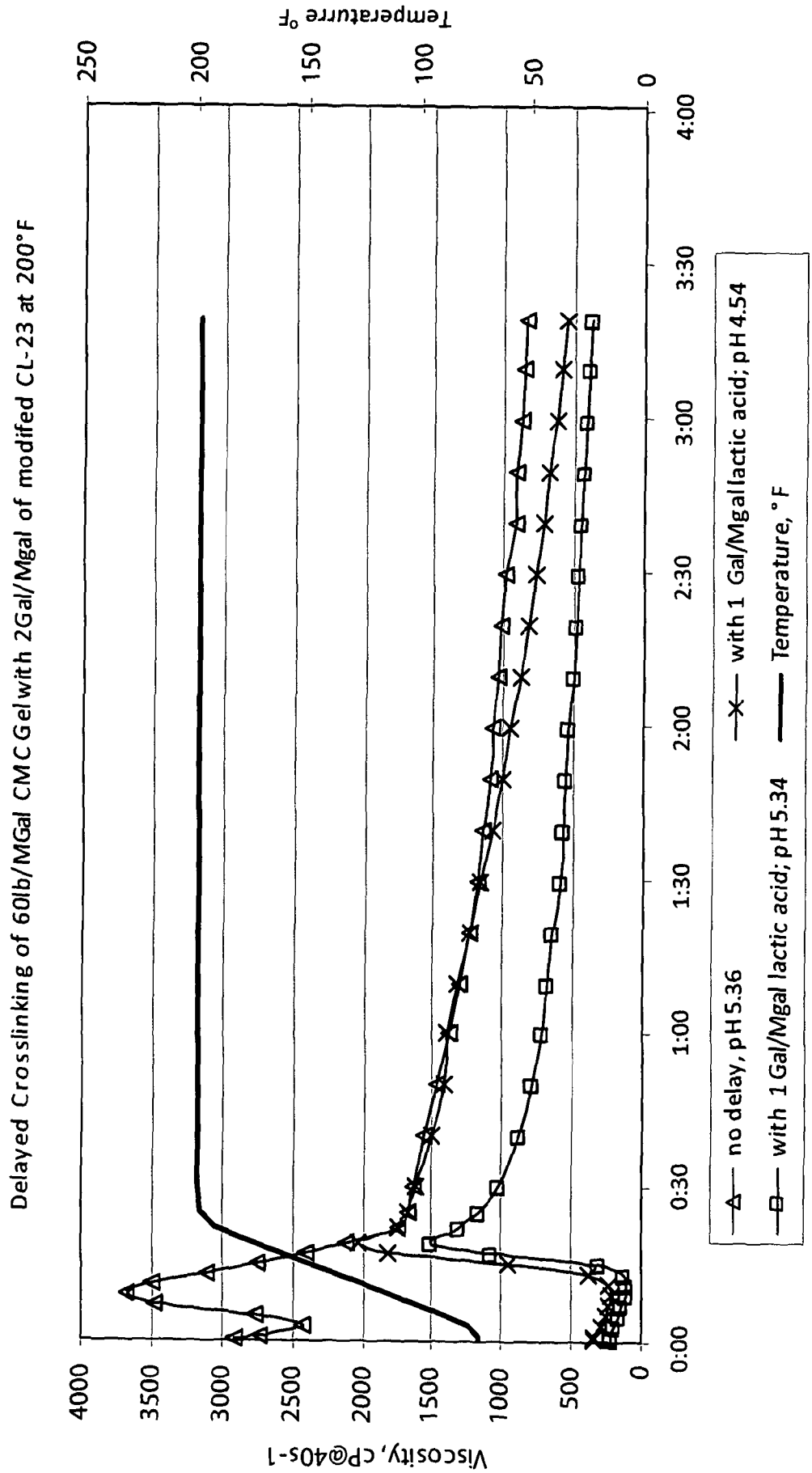

Delayed Crosslinking of 60lb/MGal CMC Gel with 2Gal/Mgal of modifed CL-23 at 200°F
Viscosity, cP@40s-1
Temperature °F
4000
3500
3000
2500
2000
1500
1000
500
0
250
200
150
100
50
0
0:00
0:30
1:00
1:30
2:00
2:30
3:00
3:30
4:00
no delay, pH 5.36
with 1 Gal/Mgal lactic acid; pH 4.54
with 1 Gal/Mgal lactic acid; pH 5.34
Temperature, °F

FIG. 6

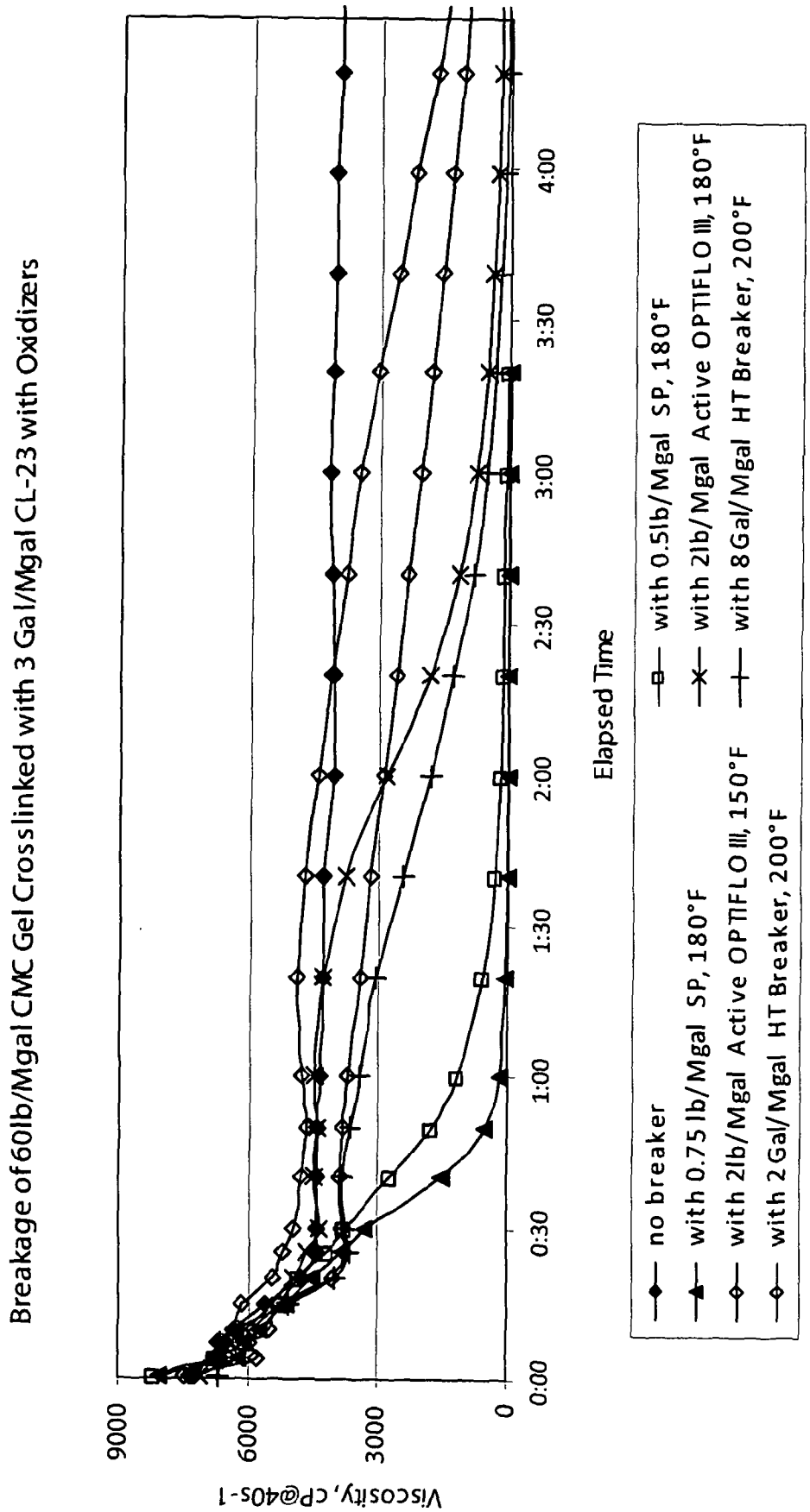

Breakage of 60lb/Mgal CMC Gel Crosslinked with 3 Gal/Mgal CL-23 with Oxidizers
Viscosity, cP@40s-1
9000
6000
3000
0
0:00
0:30
1:00
1:30
2:00
2:30
3:00
3:30
4:00
Elapsed Time
no breaker
with 0.75 lb/Mgal SP, 180°F
with 2lb/Mgal Active OPTIFLO III, 150°F
with 2 Gal/Mgal HT Breaker, 200°F
with 0.5lb/Mgal SP, 180°F
with 2lb/Mgal Active OPTIFLO III, 180°F
with 8 Gal/Mgal HT Breaker, 200°F

FIG. 7

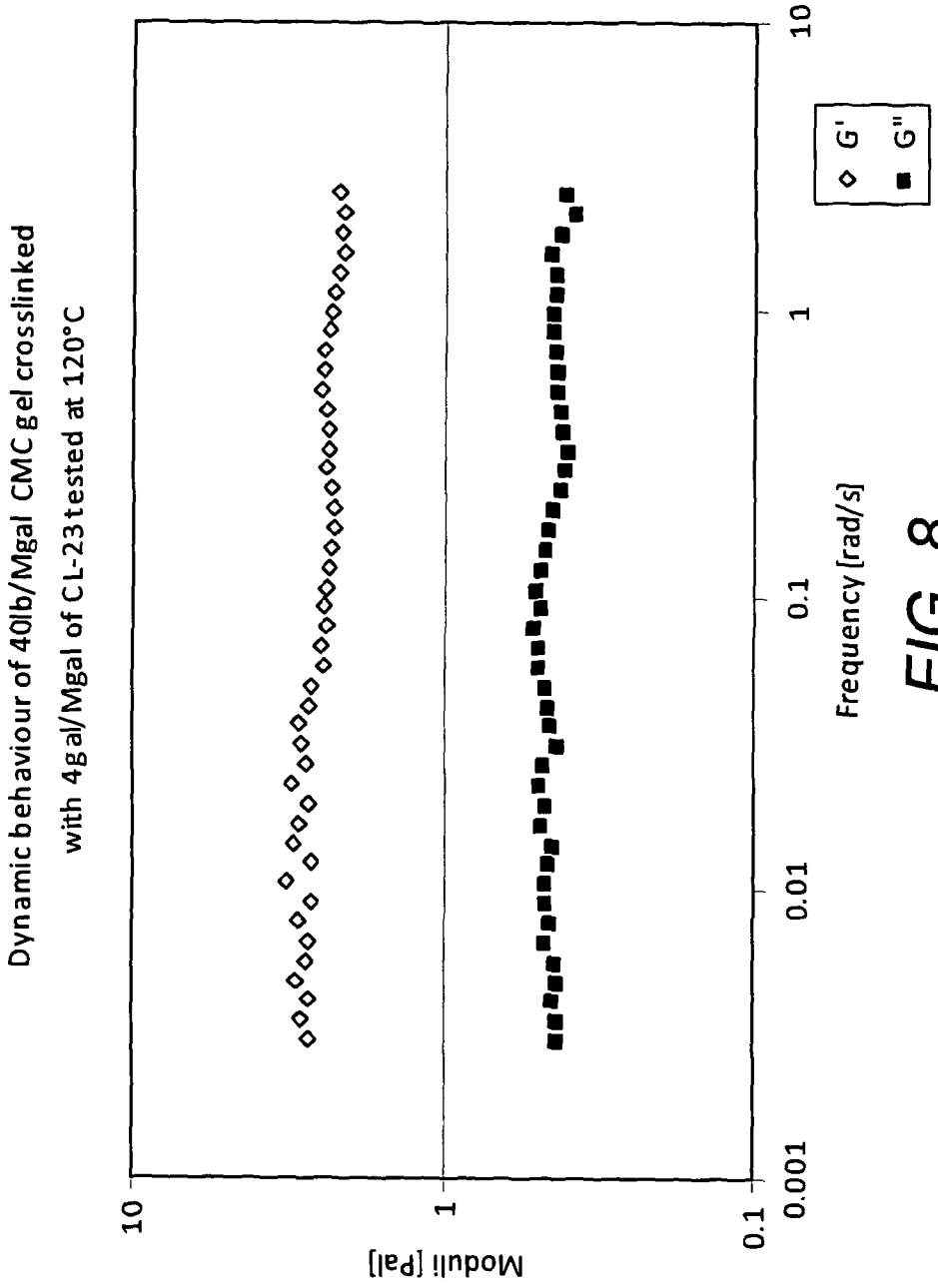

Dynamic behaviour of 40lb/Mgal CMC gel crosslinked
with 4gal/Mgal of CL-23 tested at 120°C
Moduli [Pal]
10
1
0.1
0.001
0.01
0.1
1
10
Frequency [rad/s]
G'
G"

FIG. 8

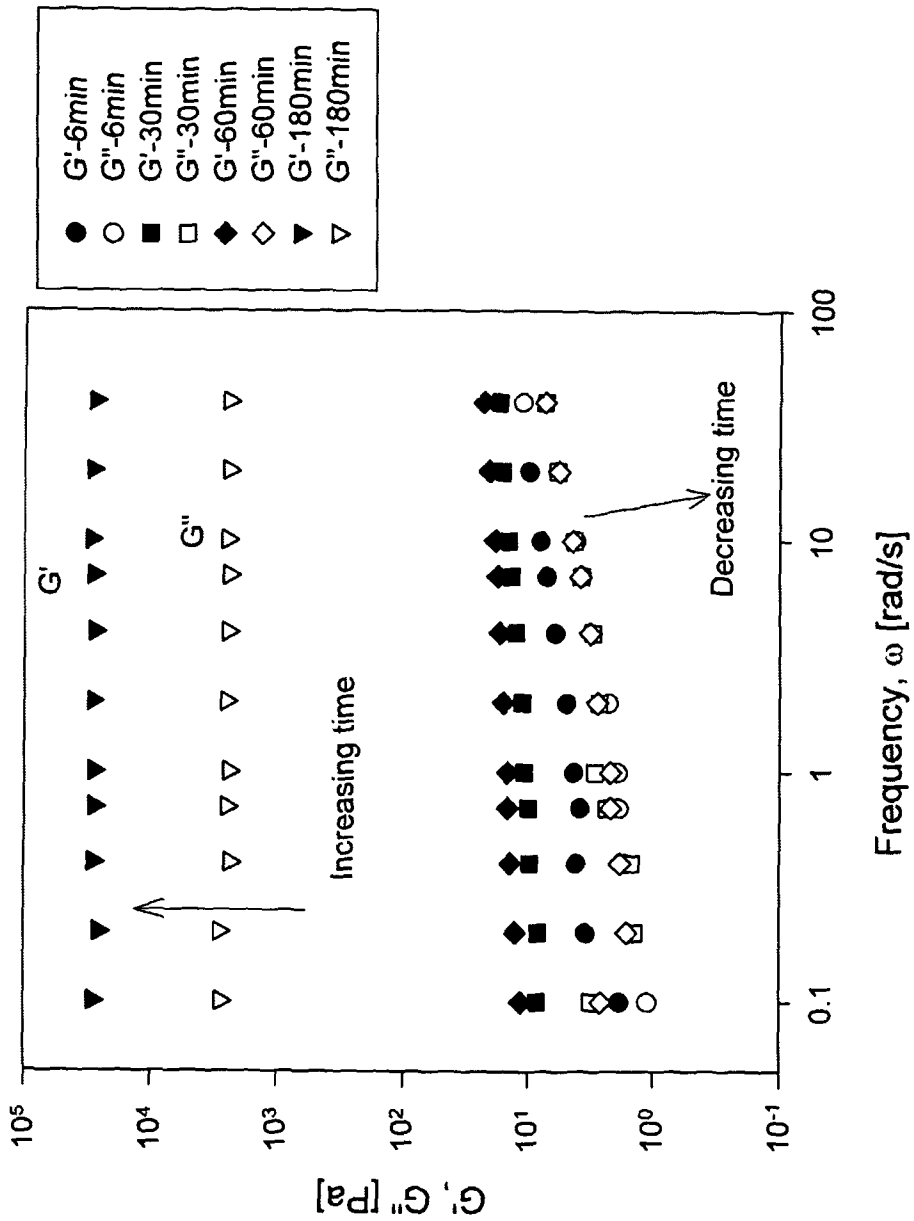
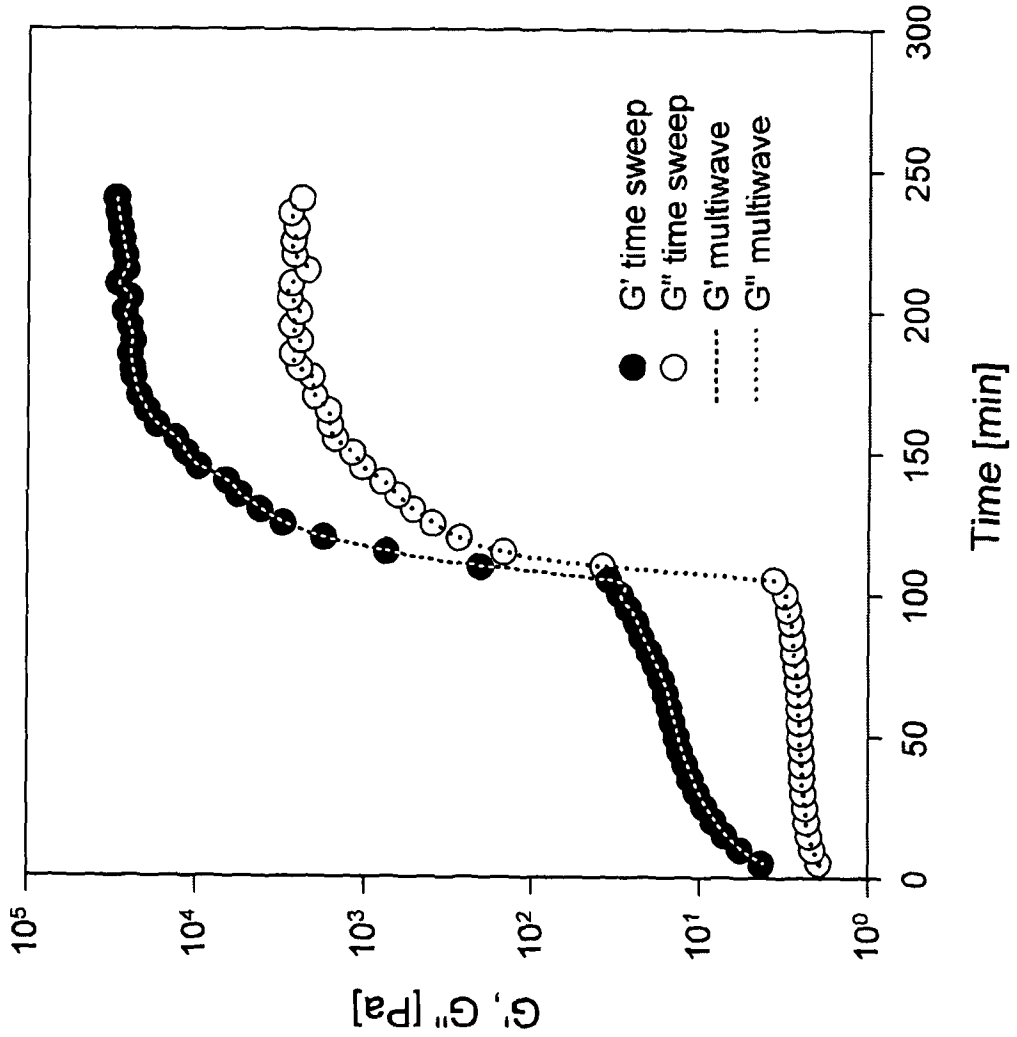

G'-6min
G"-6min
G'-30min
G"-30min
G'-60min
G"-60min
G'-180min
G"-180min
G'
G"
Increasing time
Decreasing time
G', G" [Pa]
Frequency, ω [rad/s]
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
0.1
1
10
100

FIG. 9


G', G'' [Pa]
10^5
10^4
10^3
10^2
10^1
10^0
0
50
100
150
200
250
300
Time [min]
G' time sweep
G'' time sweep
G' multiwave
G'' multiwave

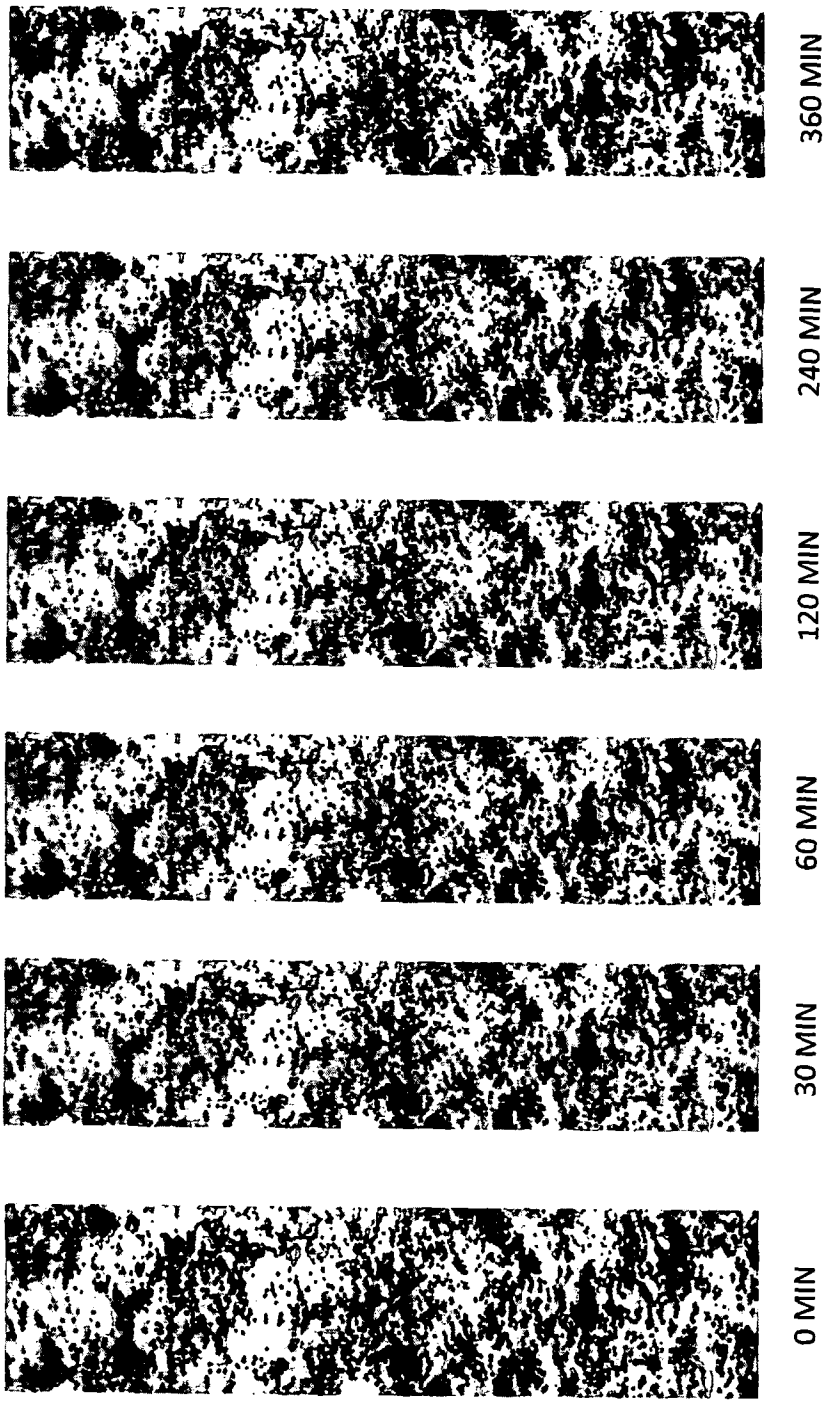


FIG. 11

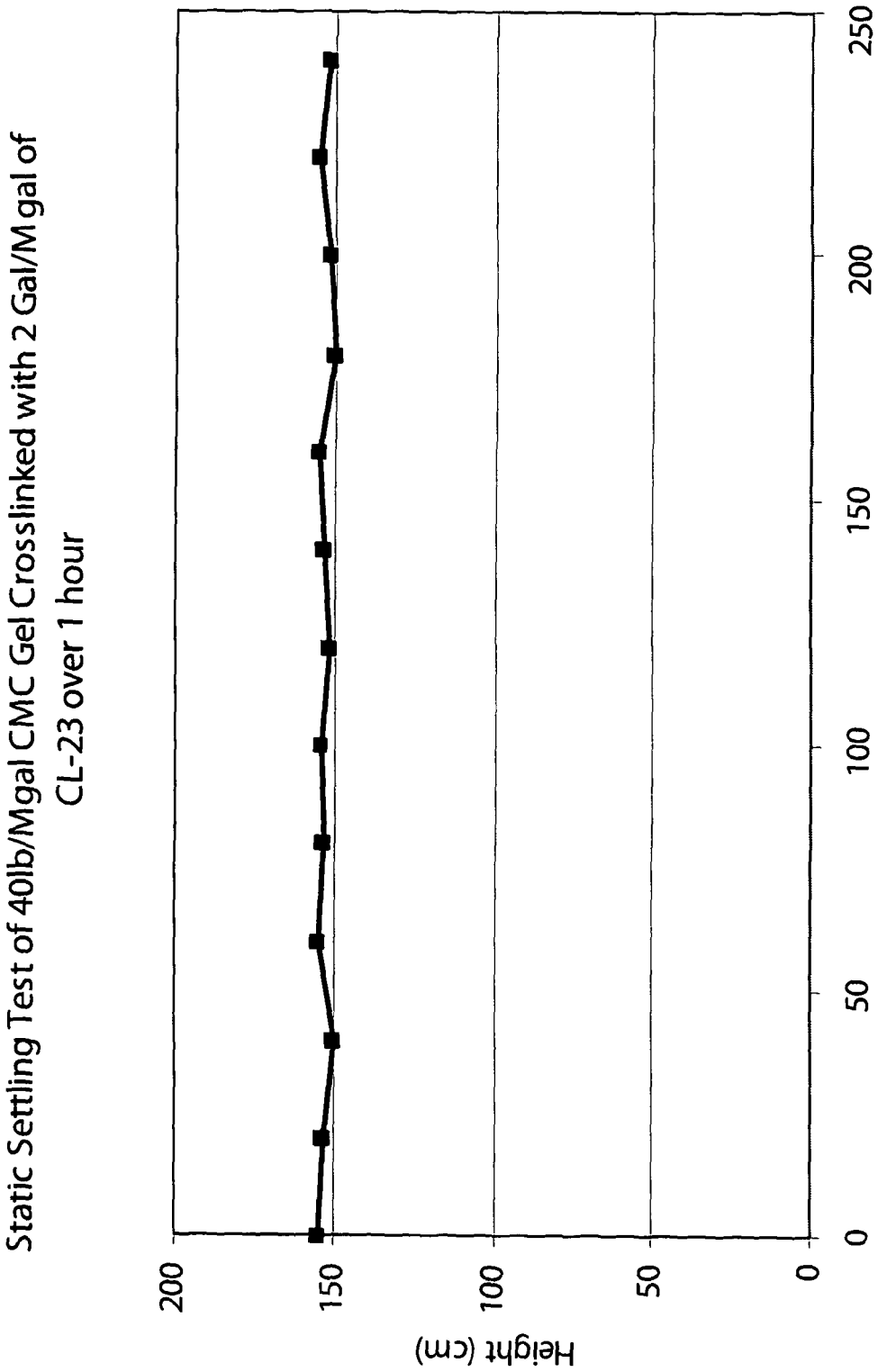

Static Settling Test of 40lb/Mgal CMC Gel Crosslinked with 2 Gal/Mgal of CL-23 over 1 hour
Height (cm)
200
150
100
50
0
Time (min)
0
50
100
150
200
250

FIG. 12

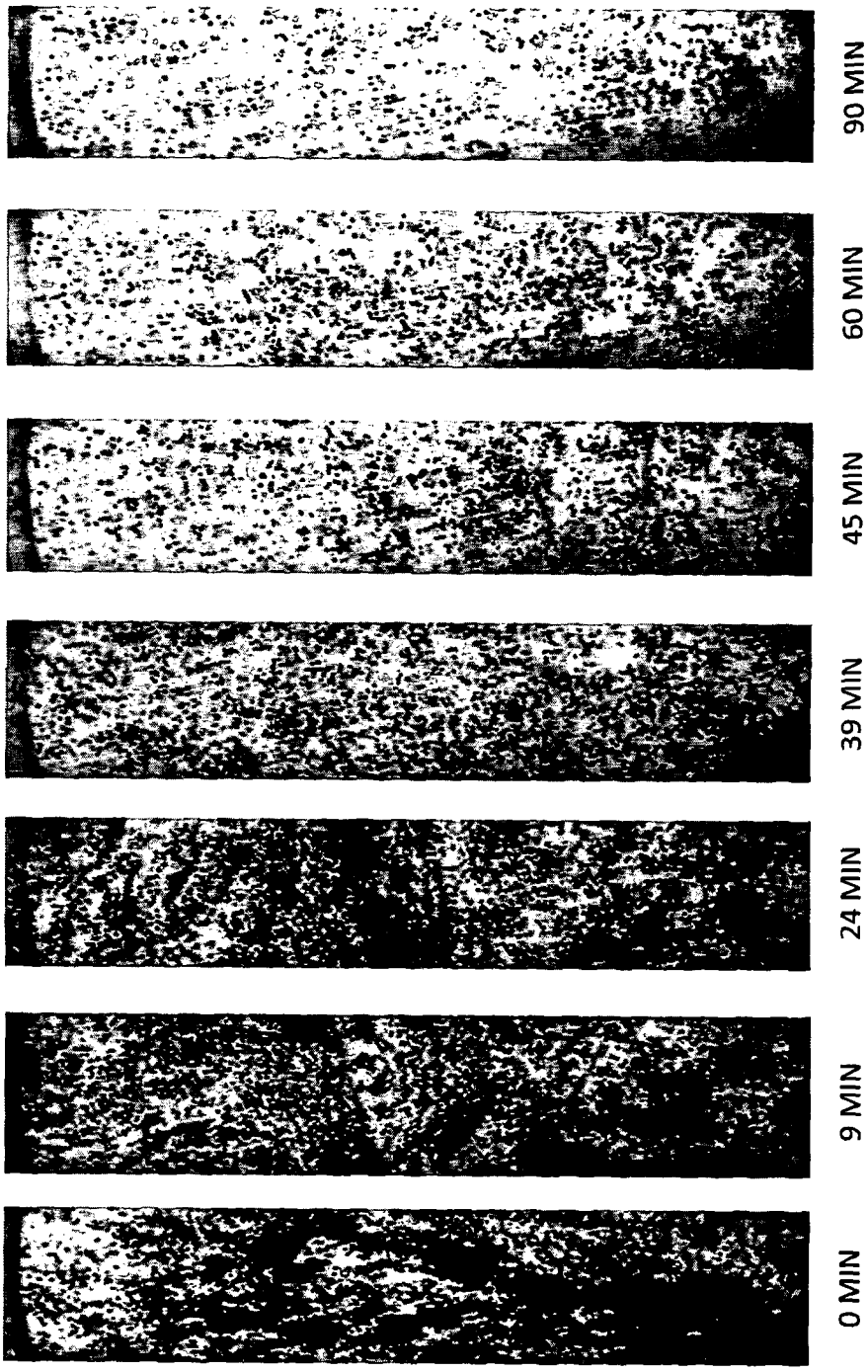


FIG. 13

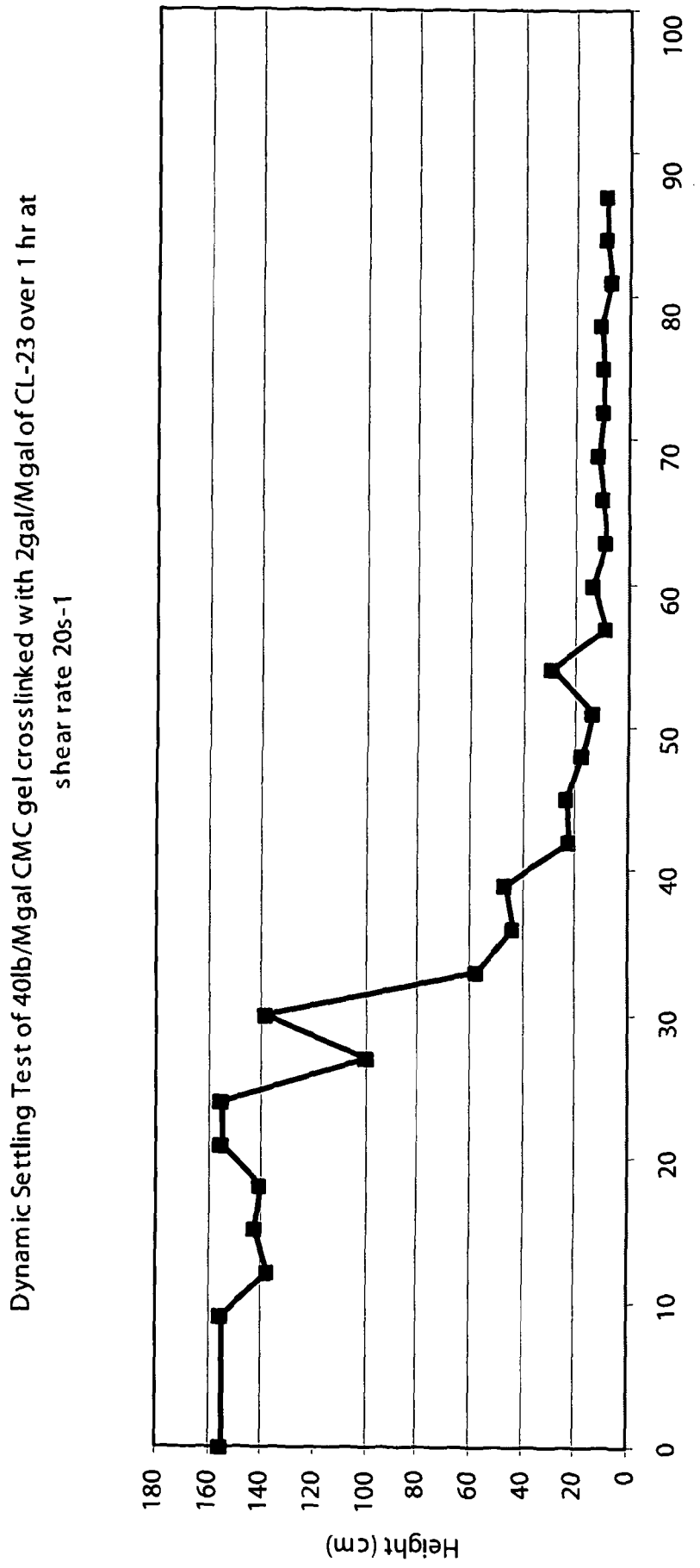

Dynamic Settling Test of 40lb/Mgal CMC gel crosslinked with 2gal/Mgal of CL-23 over 1 hr at shear rate 20s-1
Height (cm)
180
160
140
120
100
80
60
40
20
0
Time (minutes)
0
10
20
30
40
50
60
70
80
90
100

FIG. 14

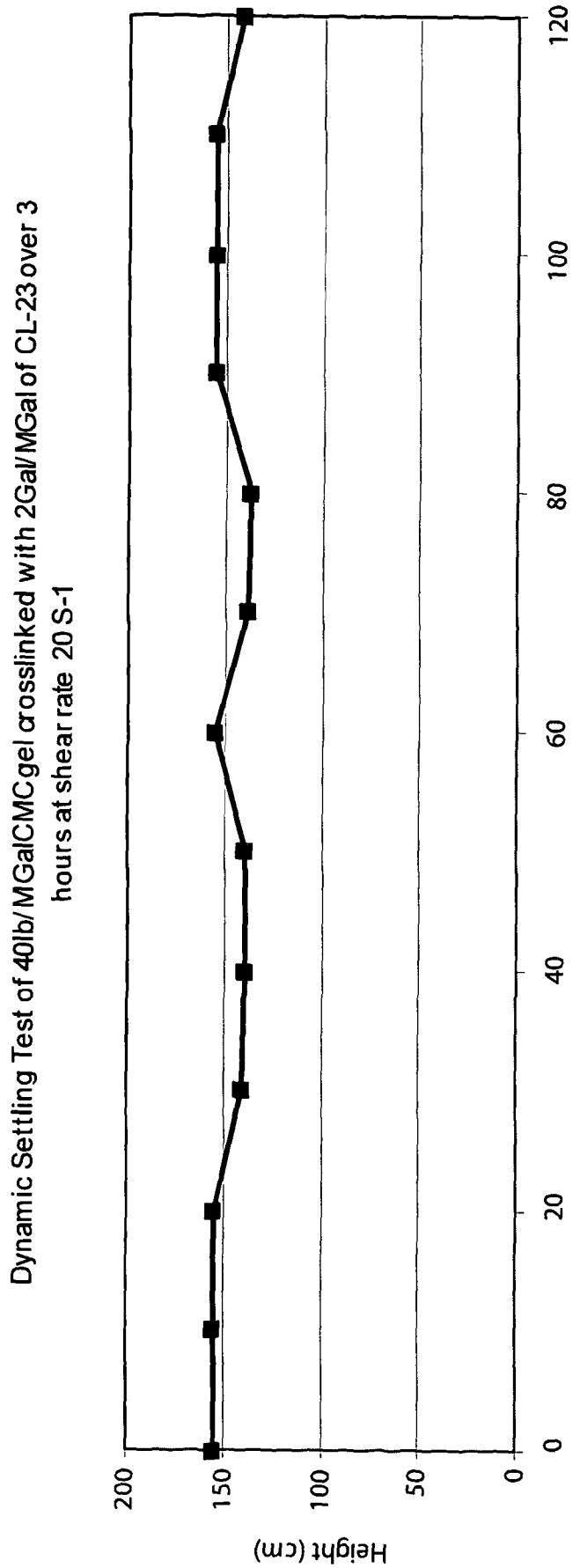

Dynamic Settling Test of 40lb/MGalCMC gel crosslinked with 2Gal/MGal of CL-23 over 3 hours at shear rate 20 S-1
Height (cm)
200
150
100
50
0
0
20
40
60
80
100
120
Time (minutes)

FIG. 15

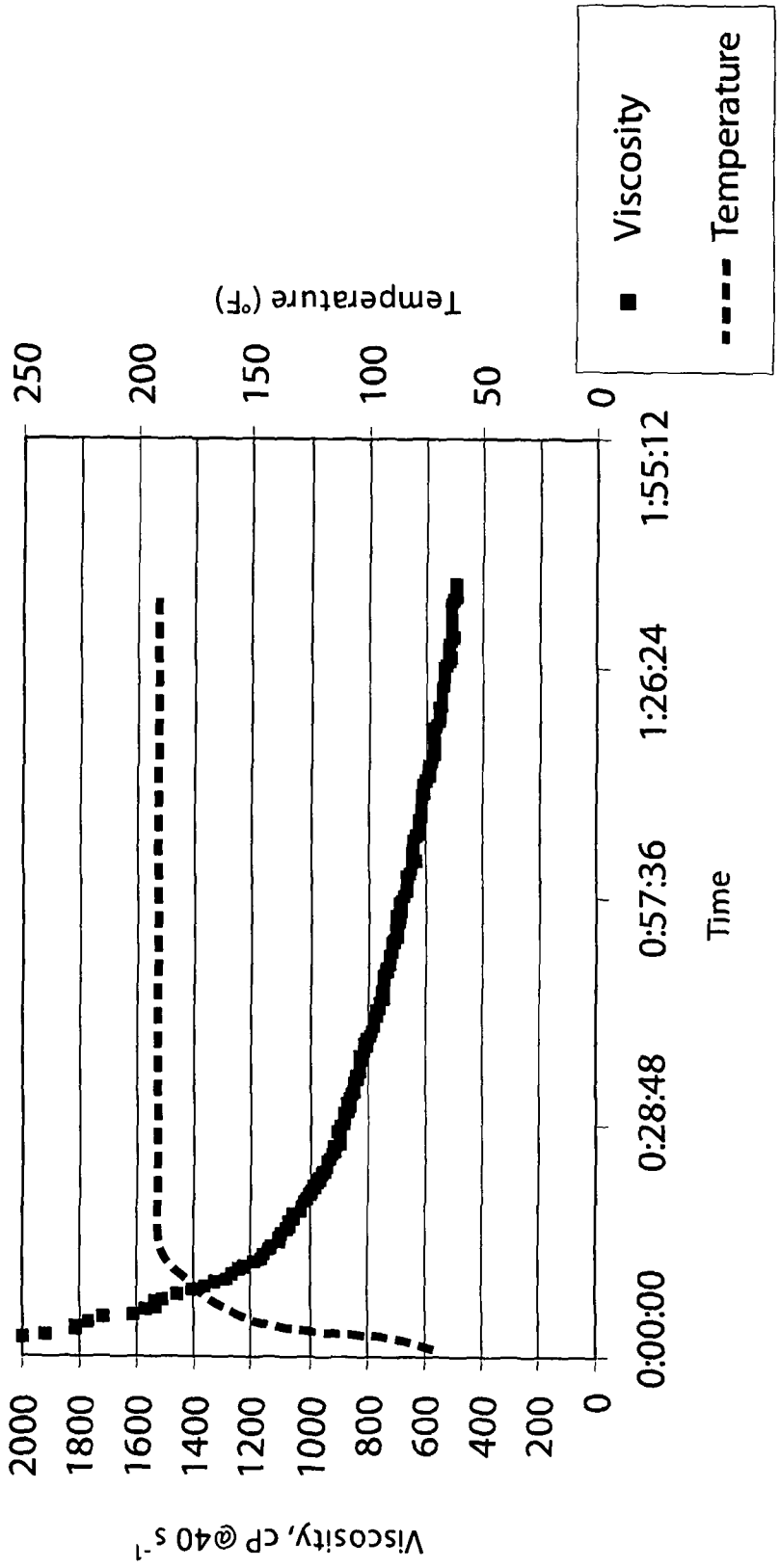

Viscosity
Temperature
Temperature (°F)
250
200
150
100
50
0
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0:00:00
0:28:48
0:57:36
1:26:24
1:55:12
Time
Viscosity, cP @40 s-1

FIG. 16

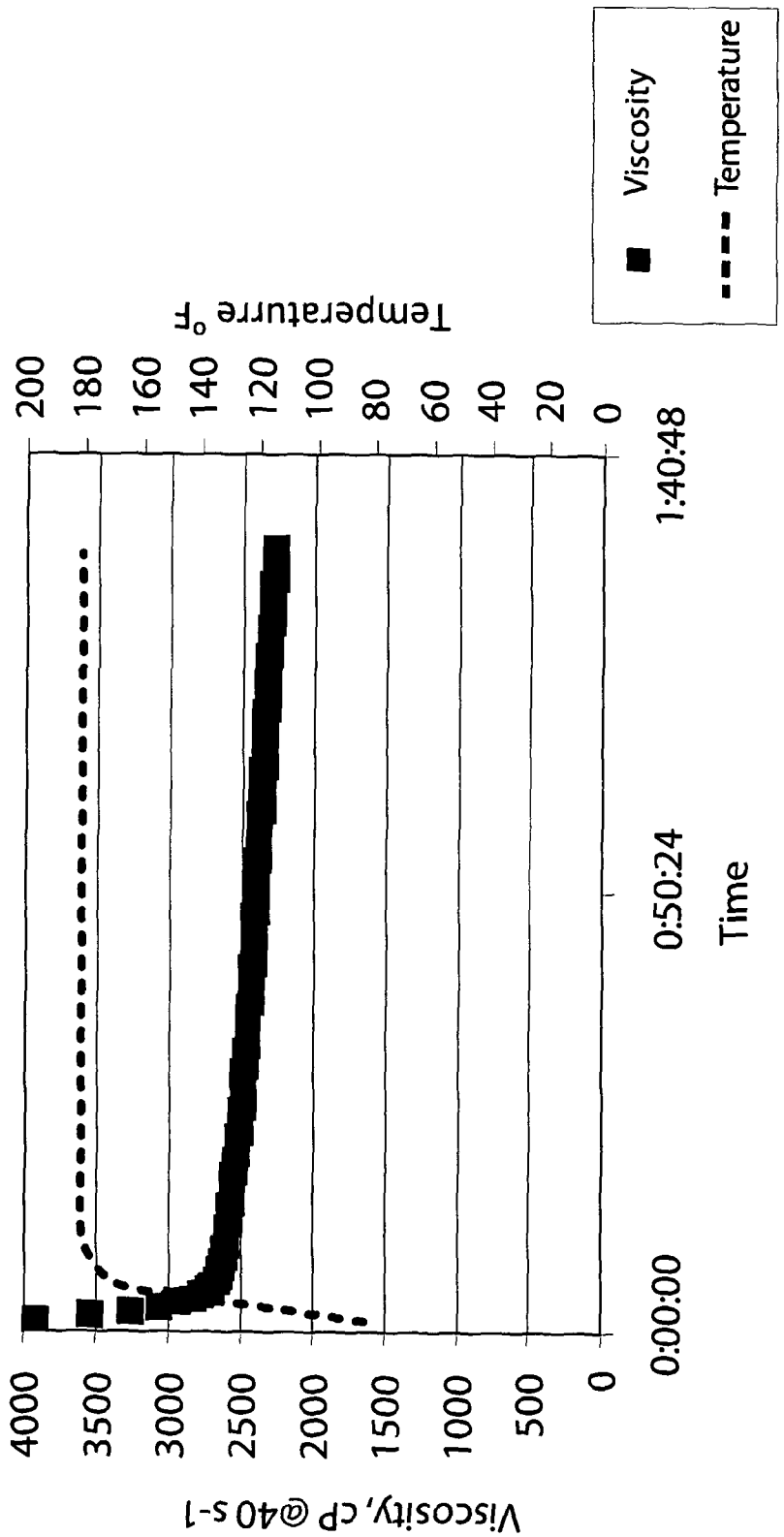

Viscosity
Temperature
Temperature °F
200
180
160
140
120
100
80
60
40
20
0
Viscosity, cP @40 s-1
4000
3500
3000
2500
2000
1500
1000
500
0
0:00:00
0:50:24
1:40:48
Time

FIG. 17

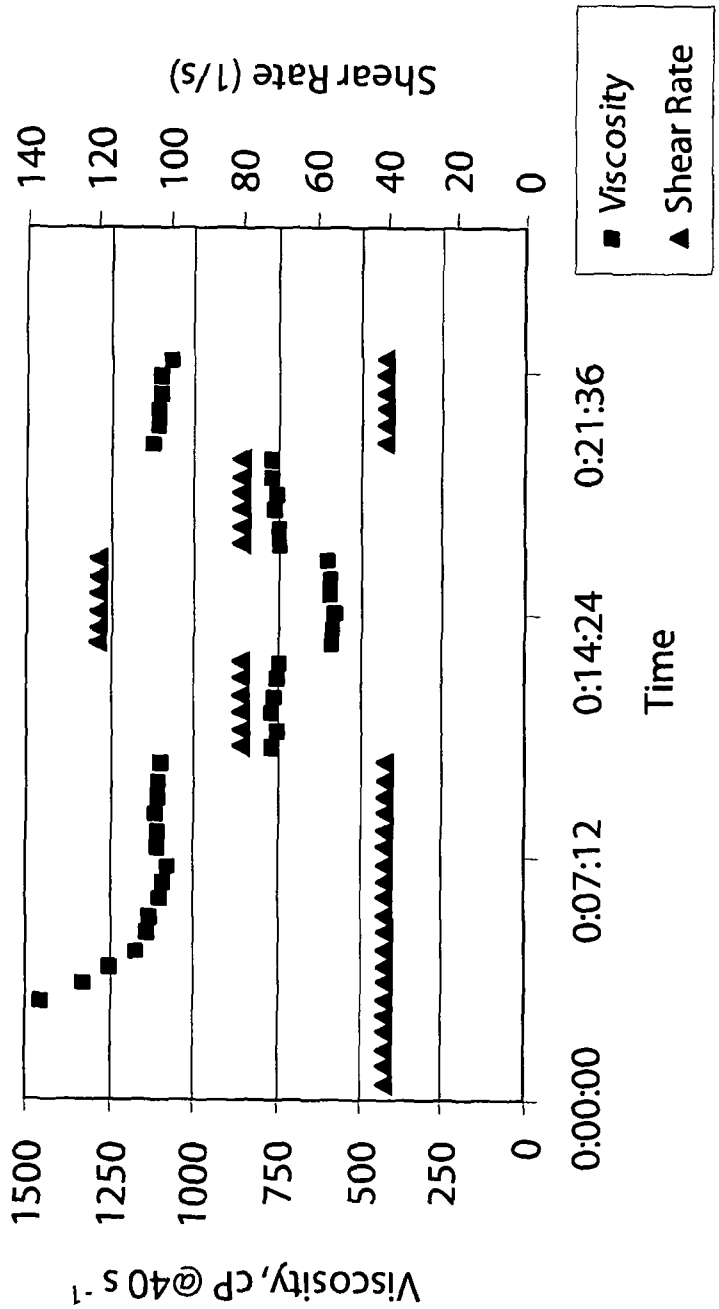

Viscosity, cP @40 s -1
1500
1250
1000
750
500
250
0
0:00:00
0:07:12
0:14:24
0:21:36
Time
Shear Rate (1/s)
140
120
100
80
60
40
20
0
Viscosity
Shear Rate

FIG. 18

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/000318

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/10 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 2010/048429 A1 (DOBSON JR JAMES W [US] ET AL) 25 February 2010 (2010-02-25) paragraphs [0008], [0925], [0028] - [0030], [0050], [0053], [0057] the whole document	1-20
X	US 5 143 157 A (HARMS WELDON M [US]) 1 September 1992 (1992-09-01) claims 1,8 the whole document	1-20
X	US 2009/203554 A1 (MONROE TERRY D [US] ET AL) 13 August 2009 (2009-08-13) paragraphs [0028], [0030] - [0034]; claim 5 the whole document	1-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2011/000318

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010048429 A1	25-02-2010	AR 070738 A1	28-04-2010
		AU 2009222091 A1	11-09-2009
		CA 2717073 A1	11-09-2009
		EP 2262870 A1	22-12-2010
		WO 2009111324 A1	11-09-2009
US 5143157 A	01-09-1992	AU 644741 B2	16-12-1993
		AU 1832292 A	24-12-1992
		CA 2071387 A1	20-12-1992
		EP 0519639 A1	23-12-1992
US 2009203554 A1	13-08-2009	AU 2009200494 A1	27-08-2009
		BR PI0900385 A2	01-12-2009