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(54) **AQUEOUS AMPHOLYTE POLYMER  
CONTAINING SOLUTIONS FOR  
SUBTERRANEAN APPLICATIONS**

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(71) Applicant: **Solvay USA Inc. - - Novicare - WSP  
Business Unit**, Castanea, PA (US)

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(72) Inventors: **HsinChen Chung**, Houston, TX (US);  
**Yuntao Thomas Hu**, The Woodlands,  
TX (US); **Xiangnan Ye**, Cypress, TX  
(US); **Narongsak Tonmukayakul**,  
Spring, TX (US); **Michael A. McCabe**,  
Duncan, OK (US); **Kevin Walter  
Frederick**, Evans City, PA (US);  
**Shih-Ruey Tom Chen**, Pittsburgh, PA  
(US); **Randy Jack Loeffler**, Carnegie,  
PA (US)

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(57) **ABSTRACT**

A aqueous solution that includes water, from 100,000 to 300,000 ppm of dissolved solids, from 0.5 to 3 gallons per thousand gallons of a water-in-oil emulsion, and an inverting surfactant. The water-in oil emulsion includes an oil phase and an aqueous phase where the oil phase is a continuous phase comprising an inert hydrophobic liquid and the aqueous phase is present as dispersed distinct particles in the oil phase. The aqueous phase contains water, a water soluble polymer, and surfactants. The water soluble polymer includes 30 to 50 weight percent of a non-ionic monomer, 5 to 15 weight percent of a sulfonic acid containing monomer, and 40 to 60 weight percent of a cationic monomer. The water soluble polymer makes up from 10 to 35 weight percent of the water-in-oil emulsion.

**Related U.S. Application Data**

(60) Provisional application No. 61/829,609, filed on May 31, 2013.

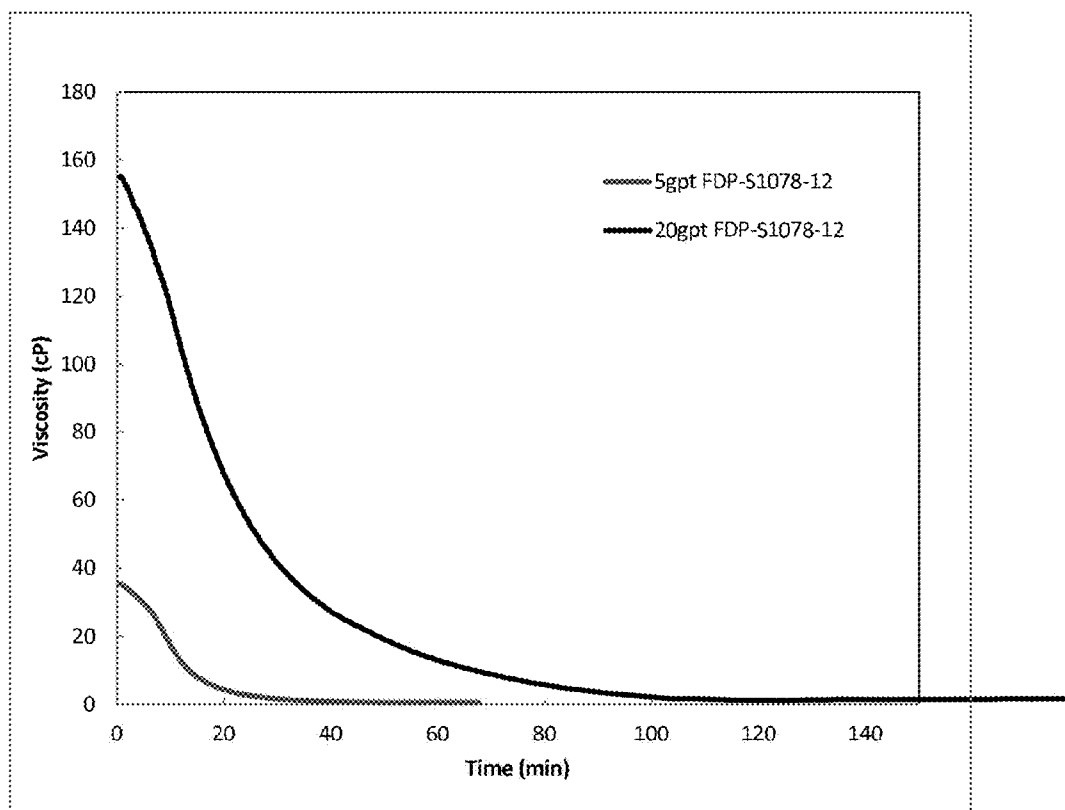
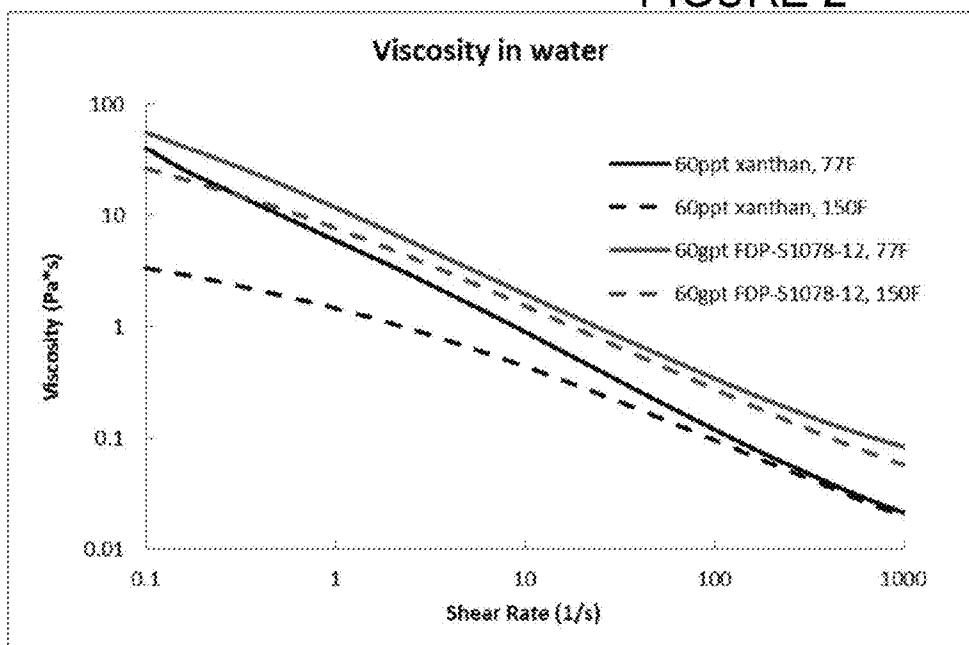


FIGURE 1

FIGURE 2



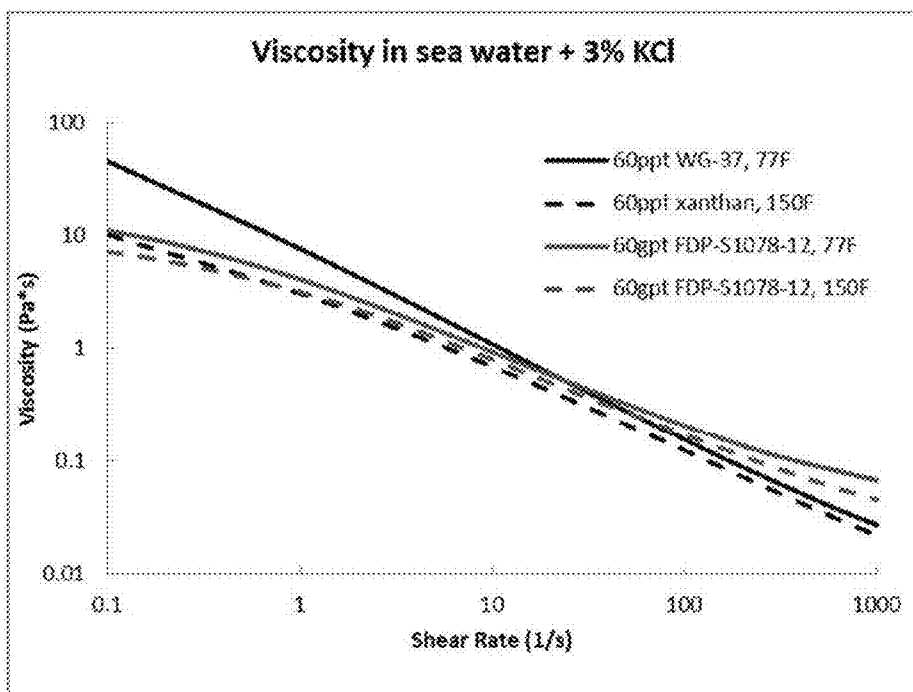
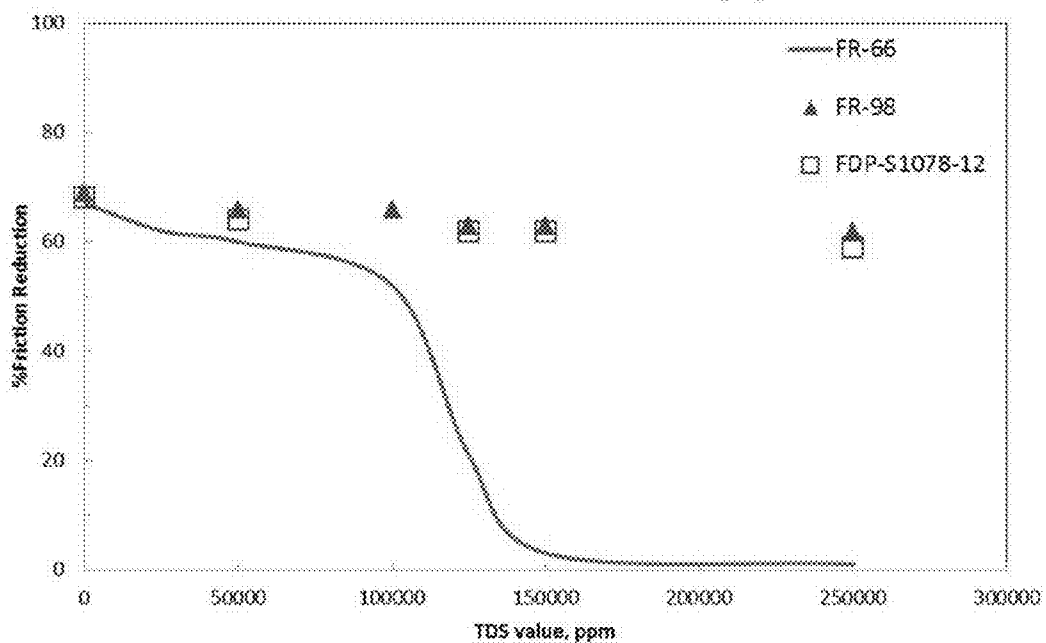


FIGURE 3

FIGURE 4



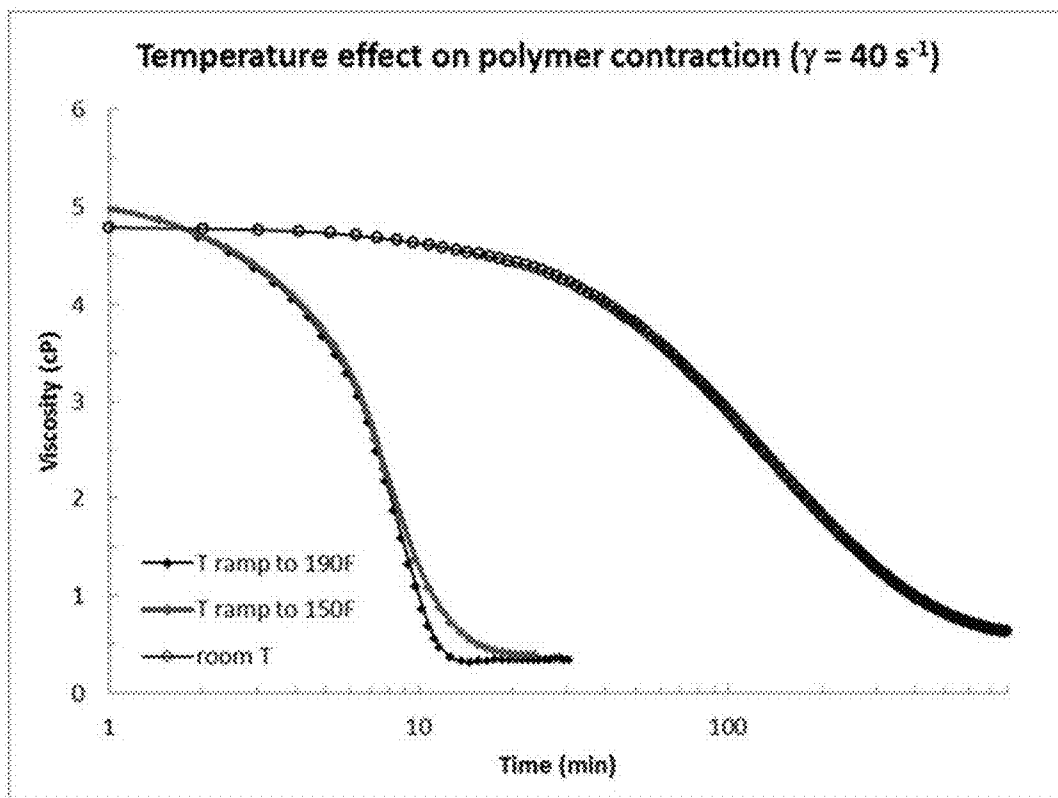
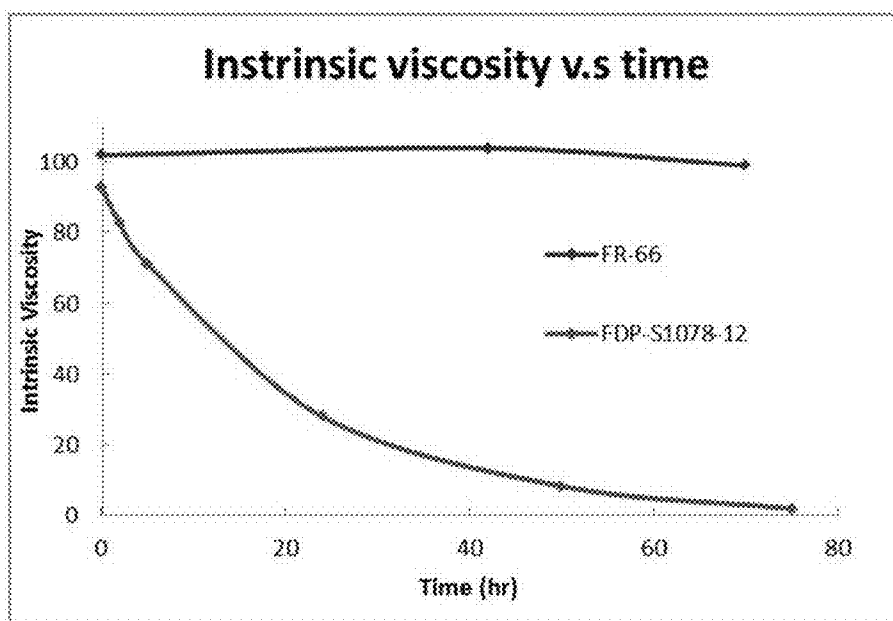


FIGURE 5

FIGURE 6



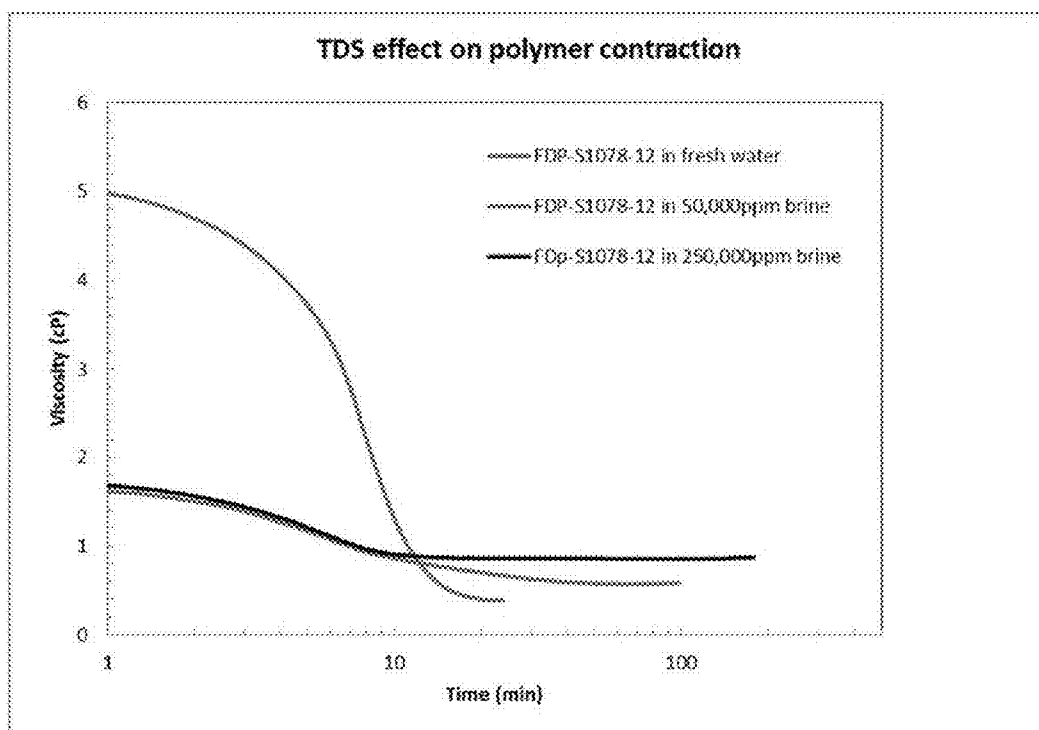


FIGURE 7

## AQUEOUS AMPHOLYTE POLYMER CONTAINING SOLUTIONS FOR SUBTERRANEAN APPLICATIONS

### REFERENCE TO RELATED APPLICATION

**[0001]** This application claims the benefit of priority of U.S. Provisional Application Ser. No. 61/829,609 filed May 31, 2013 entitled "Ampholyte Polymeric Compounds in Subterranean Applications" which is herein incorporated by reference in its entirety.

### BACKGROUND OF THE INVENTION

**[0002]** 1. Field of the Invention

**[0003]** At least some of the exemplary embodiments described herein relate to compositions for treating subterranean zones. The compositions include aqueous solutions that contain water soluble polymers in a water-in-oil emulsion form and high total dissolved solids.

**[0004]** 2. Description of the Prior Art

**[0005]** Aqueous treatment fluids may be used in a variety of subterranean treatments. Such treatments include, but are not limited to, drilling operations, 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.

**[0006]** Viscous gelled fracturing fluids are commonly utilized in the hydraulic fracturing of subterranean zones penetrated by well bores to increase the production of hydrocarbons from the subterranean zones. That is, a viscous fracturing fluid is pumped through the well bore into a subterranean zone to be stimulated at a rate and pressure such that fractures are formed and extended into the subterranean zone. The fracturing fluid also carries particulate proppant material, e.g., graded sand, into the formed fractures. The proppant material is suspended in the viscous fracturing fluid so that the proppant material is deposited in the fractures when the viscous fracturing fluid is broken and recovered. The proppant material functions to prevent the fractures from closing whereby conductive channels are formed through which produced fluids can flow to the well bore.

**[0007]** An example of a stimulation operation utilizing an aqueous treatment fluid is hydraulic fracturing. In some instances, a fracturing treatment involves pumping a proppant-free, aqueous treatment fluid (known as a pad fluid) into a subterranean formation faster than the fluid can escape into the formation so that the pressure in the formation rises and the formation breaks, creating or enhancing one or more fractures. Enhancing a fracture includes enlarging a pre-existing fracture in the formation. Once the fracture is formed or enhanced, proppant particulates are generally placed into the fracture to form a proppant pack that may prevent the fracture from closing when the hydraulic pressure is released, forming conductive channels through which fluids may flow to the well bore.

**[0008]** During the pumping of the aqueous treatment fluid into the well bore, a considerable amount of energy may be lost due to friction between the aqueous treatment fluid in turbulent flow and the formation and/or tubular goods (e.g., pipes, coiled tubing, etc.) disposed within the well bore. As a result of these energy losses, additional horsepower may be necessary to achieve the desired treatment. To reduce these

energy losses, friction reducing polymers have heretofore been included in aqueous treatment fluids. The friction reducing polymer should reduce the frictional losses due to friction between the aqueous treatment fluid in turbulent flow and the tubular goods and/or the formation.

**[0009]** Many friction reducing polymers show a reduced performance in the presence of low molecular weight additives, such as acids, bases, and salts. Ionically-charged polymers are particularly susceptible. For example, polymers containing acrylate-type monomers, either added as a copolymer or hydrolyzed from polyacrylamide, have a reduced compatibility with high calcium brines. The additives screen the charges on the polymer backbone which decreases the hydrodynamic radius of the polymer. With the decrease in effective polymer length, the friction reduction also decreases.

**[0010]** Hydraulic fracturing has been a boon to the oil and gas industry. Many oil and gas wells have been made more productive due to the procedure. However, the hydraulic fracturing business is now facing increasing scrutiny and government regulation. In addition, large volumes of water are required for hydraulic fracturing operations. Fresh water may be a limiting factor in some areas. A treatment solution that can use a variety of water sources, such as produced water from the formation or flowback water after a well treatment, could significantly enhance the field applicability.

**[0011]** The relatively high polymer usage in subterranean treatment methods can result in significant formation damage. Further, when the treatment fluid is recycled above ground, the high levels of high molecular weight polymers in the fluid can lead to flocculation in above ground fluid recycle operations such as terminal upsets.

**[0012]** There is an ongoing need to develop treatment solutions that have effective friction reduction to minimize energy loss but yet have sufficient viscosity for proppant-carrying capacity, especially in high brine situations, while being safe and environmentally friendly.

### SUMMARY OF THE INVENTION

**[0013]** The present invention is directed to an aqueous solution that includes water, from 100,000 to 300,000 ppm of dissolved solids, from 0.5 to 3 gallons per thousand gallons of a water-in-oil emulsion, and an inverting surfactant. The water-in-oil emulsion includes an oil phase and an aqueous phase where the oil phase is a continuous phase comprising an inert hydrophobic liquid and the aqueous phase is present as dispersed distinct particles in the oil phase. The aqueous phase contains water, a water soluble polymer, and surfactants. The water soluble polymer includes 30 to 50 weight percent of a non-ionic monomer, 5 to 15 weight percent of a sulfonic acid containing monomer, and 40 to 60 weight percent of a cationic monomer. The water soluble polymer makes up from 10 to 35 weight percent of the water-in-oil emulsion.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0014]** The following figures are included to illustrate certain aspects of the exemplary embodiments described herein, and should not be viewed as exclusive embodiments. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0015] FIG. 1 provides a graph of the viscosity of an ampholyte polymeric compound at various concentrations over time at an elevated temperature.

[0016] FIG. 2 provides a graph comparing the viscosity of an ampholyte polymeric compound and a traditional viscosifier in water.

[0017] FIG. 3 provides a graph comparing the viscosity of an ampholyte polymeric compound and a traditional viscosifier in a high TDS water.

[0018] FIG. 4 provides a graph of percent friction reduction at various salinities for three friction reducing additives including one ampholyte polymeric compound.

[0019] FIG. 5 provides a graph of viscosity measurements over time at various temperatures for a fluid comprising an ampholyte polymeric compound.

[0020] FIG. 6 provides a graph comparing the intrinsic viscosity over time for a fluid comprising an ampholyte polymeric compound and a fluid comprising a traditional friction reducing agent.

[0021] FIG. 7 provides a graph of viscosity measurements over time at various TDS concentrations for fluids comprising an ampholyte polymeric compound.

#### DETAILED DESCRIPTION

[0022] Other than in the operating examples, or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc. used in the specification and claims are to be understood as modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the exemplary embodiments described herein. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0023] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the exemplary embodiments described herein are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0024] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10; that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. Because the disclosed numerical ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

[0025] As used herein, the term “ampholyte” refers to a compound having both a positive and a negative charge. The ampholyte polymers described herein include nonionic monomers, cationic monomers, and sulfonic acid-containing monomers.

[0026] As used herein, the term “polymer” is meant to encompass oligomer, and includes, without limitation, both homopolymers and copolymers.

[0027] As used herein, the term “copolymer,” as used herein, is not limited to polymers containing two types of monomeric units, but includes any combination of polymers, e.g., terpolymers, tetrapolymers, and the like.

[0028] As used herein, “total dissolved solids” (“TDS”) refers to a measure of the combined content of all inorganic and organic substances contained in water including ionized solids in the water.

[0029] The exemplary embodiments described herein provide, in some instances, an aqueous ampholyte polymer solutions that includes water, from 100,000 to 300,000 ppm of dissolved solids, from 0.5 to 3 gallons per thousand gallons of a water-in-oil emulsion, and an inverting surfactant. In some instances, the water-in oil emulsion includes an oil phase and an aqueous phase where the oil phase is a continuous phase comprising an inert hydrophobic liquid and the aqueous phase is present as dispersed distinct particles in the oil phase. In some instances, the aqueous phase contains water, a water soluble polymer (also referred to as an ampholyte polymeric compound), and surfactants. In some instances, the water soluble polymer includes 30 to 50 weight percent of a non-ionic monomer, 5 to 15 weight percent of a sulfonic acid containing monomer, and 40 to 60 weight percent of a cationic monomer. In some instances, the water soluble polymer makes up from 10 to 35 weight percent of the water-in-oil emulsion.

[0030] The ampholyte polymers described herein (also referred to as water soluble polymers) are suitable for friction reduction in treatment fluids, including in high TDS treatment fluids (e.g., treatment fluids with saltwater or brackish water base fluids). Further, the ampholyte polymers described herein advantageously provide for single-component friction reduction agents that reduce implementation complexity as compared to the multi-component friction reducing systems described above. Together, these properties and advantages provide for friction reducing agents having enhanced operational efficacy, reduce the energy requirement, and reduce the cost of the treatment.

[0031] Further, the aqueous ampholyte polymer solutions described herein may advantageously break over time with the use of little or no breaker. Without being limited by theory, it is believed that, at least some of the monomeric units of the ampholyte polymers may at least partially hydrolyze, which in turn may cause the ampholyte polymeric compound to contract and reduce its friction reducing effect. As used herein, the terms “partially hydrolyze,” “partially hydrolysis,” and the like refer to hydrolysis of at least some of the monomeric units of a polymeric compound (e.g., ampholyte polymers described herein). Partial hydrolysis and polymeric contraction of an ampholyte polymeric compound described herein may advantageously allow wellbore operations to be performed with minimal amounts of breaker in the treatment fluid and/or without the need for a subsequent breaking treatment (and perhaps in some instances, without any breaker or need for subsequent breaking treatments), which reduces the cost and time associated with the wellbore operations.

[0032] The aqueous ampholyte polymer solutions of the exemplary embodiments described herein may, in some embodiments, include water, dissolved solids, and a water-in-oil emulsion that contains a copolymer.

**[0033]** The water-in-oil emulsions described herein include an oil phase, an aqueous phase and surfactants.

**[0034]** In some embodiments, the oil phase (O) and the aqueous phase (A) can be present at an O/A ratio, based on the volume of each phase of from at least about 1:8, in some cases at least about 1:6 and in other cases at least about 1:4 and can be up to about 10:1, in some cases up to about 8:1 and in other cases up to about 6:1. Without being limited by theory, it is believed that when the O/A ratio is too oil heavy, the polymer may be too concentrated in the aqueous phase. In some instances, when the O/A ratio is too water heavy, the emulsion may become unstable and prone to separate. The O/A ratio can be any ratio or range between any of the ratios recited above.

**[0035]** In the present water-in-oil emulsion, the oil phase is present as a continuous phase and includes an inert hydrophobic liquid. The inert hydrophobic liquid can include, as non-limiting examples, paraffinic hydrocarbons, naphthenic hydrocarbons, aromatic hydrocarbons, benzene, xylene, toluene, mineral oils, kerosenes, naphthas, petrolatums, branch-chain isoparaffinic solvents, branch-chain hydrocarbons, saturated, linear, and/or branched paraffin hydrocarbons and combinations thereof. Particular non-limiting examples include natural, modified or synthetic oils such as the branch-chain isoparaffinic solvent available as ISOPAR® M and EXXATE® available from ExxonMobile Corporation, Irving Tex., a narrow fraction of a branch-chain hydrocarbon available as KENSOL® 61 from Witco Chemical Company, New York, N.Y., mineral oil, available commercially as BLANDOL® from Witco, CALUMET™ LVP-100 available from Calumet Specialty Products, Burnham, Ill., DRAKEOL® from Penreco Partnership, Houston, Tex., MAGIESOL® from Magie Bros., Oil City, Pa. and vegetable oils such as canola oil, coconut oil, rapeseed oil and the like.

**[0036]** The inert hydrophobic liquid is present in the water-in-oil emulsion in an amount sufficient to form a stable emulsion. In some embodiments, the inert hydrophobic liquid can be present in the water-in-oil emulsions in an amount in the range of from about 15% to about 80% by weight.

**[0037]** In some embodiments, the inert hydrophobic liquid is present in the water-in-oil emulsion at a level of at least about 15, in some cases at least about 17.5, in other cases at least about 20, and in some instances at least about 22.5 weight percent based on the weight of the water-in-oil emulsion and can be present at up to about 40, in some cases up to about 35, in other cases up to about 32.5 and in some instances up to about 30 weight percent based on the weight of the water-in-oil emulsion. The total amount of inert hydrophobic liquid in the water-in-oil emulsion can be any value or can range between any of the values recited above.

**[0038]** Any suitable water-in-oil emulsifier can be used as the one or more surfactants used to make the water soluble polymer containing water-in-oil emulsion used in the exemplary embodiments described herein. In some embodiments, the surfactants include those having an HLB (hydrophilic-lipophilic balance) value between 2 and 10 in some cases between 3 and 9 and in other cases between 3 and 7.

**[0039]** As used herein, HLB is calculated using the art known method of calculating a value based on the chemical groups of the molecule. The method uses the following equation:

$$HLB=7+m*Hh+n*HI$$

where m represents the number of hydrophilic groups in the molecule, Hh represents the value of the hydrophilic groups, n represents the number of lipophilic groups in the molecule and HI represents the value of the lipophilic groups.

**[0040]** Non-limiting examples of suitable surfactants include: fatty acid esters of mono-, di- and polyglycerols, for instance the monoleate, the dioleate, the monostearate, the distearate and the palmitostearate. These esters can be prepared, for example, by esterifying mono-, di- and polyglycerols, or mixtures of polyhydroxylated alcohols such as ethylene glycol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,2,4-butanetriol, glycerol, trimethylolpropane, sorbitol, neopentyl glycol and pentaerythritol; fatty acid esters of sorbitan, for instance sorbitan monoleate, sorbitan dioleate, sorbitan trioleate, sorbitan monostearate and sorbitan tristearate; fatty acid esters of mannitol, for instance mannitol monolaurate or mannitol monopalmitate; fatty acid esters of pentaerythritol, for instance pentaerythritol monomyristate, pentaerythritol monopalmitate and pentaerythritol dipalmitate; fatty acid esters of polyethylene glycol sorbitan, more particularly the monooleates; fatty acid esters of polyethylene glycol mannitol, more particularly the monooleates and trioleates; fatty acid esters of glucose, for instance glucose monooleate and glucose monostearate; trimethylolpropane distearate; the products of reaction of isopropylamide with oleic acid; fatty acid esters of glycerol sorbitan; ethoxylated alkylamines; sodium hexadecyl phthalate; sodium decyl phthalate; and oil-soluble alkanolamides.

**[0041]** In some embodiments, the surfactants can include ethoxylated nonionic surfactants, guerbet alcohol ethoxylate, and mixtures thereof. Specific examples include, but are not limited to tall oil fatty acid diethanolamine, such as those available as AMADOL® 511, from Akzo Nobel Surface Chemistry, Chicago, Ill.; polyoxyethylene (5) sorbitan monooleate, available as TWEEN® 81, from Uniqema, New Castle, Del.; sorbinate monooleate, available as SPAN® 80 from Uniquena, and ALKAMULS® SMO, from Rhone Poulenc, Inc., Paris, France.

**[0042]** In some embodiments, the surfactants can be present at a level of at least about 0.1, in some instances at least about 0.25, in other instances at least about 0.5, in some cases at least about 0.75 and in other cases at least about 1 weight percent of the water-in-oil emulsion. Without being limited by theory, it is believed that when the amount of surfactants is too low, the aqueous phase may not be adequately dispersed in the oil phase and/or the water-in-oil emulsion may tend to separate into oil and aqueous phases. In some embodiments, the amount of surfactants can be up to about 7, in some cases up to about 5, and in other cases up to about 2.5 weight percent of the water-in-oil emulsion. The amount of surfactants in the water-in-oil emulsion can be any value or can range between any of the values recited above.

**[0043]** The aqueous phase is present in the water-in-oil emulsion as a dispersed phase of distinct particles in the oil phase and includes water and a water soluble polymer. In some embodiments, the aqueous phase in total can be present in the present water-in-oil emulsion polymer composition at a level of at least about 60, in some instances at least about 65, in some cases at least about 67.5, and in other cases at least about 70 weight percent based on the weight of the water-in-oil emulsion and can be present at up to about 85, in some cases up to about 82.5, in other cases up to about 80 and in some instances up to about 77.5 weight percent based on the weight of the water-in-oil emulsion. The total amount of aqueous phase in the water-in-oil emulsion can be any value or can range between any of the values recited above.

**[0044]** In some embodiments, the water soluble polymer is present at a level of at least about 10, in some cases at least



about 15, and in other cases at least about 25 weight percent based on the weight of the water-in-oil emulsion and can be present at up to about 33, in some cases up to about 35, in other cases up to about 37 and in some instances up to about 40 weight percent based on the weight of the water-in-oil emulsion. When the amount of water soluble polymer is too low, the use of the water-in-oil emulsion to treat a portion of a subterranean formation may be uneconomical. However, when the amount of water soluble polymer is too high, the performance of the water soluble polymer may be less than optimum. The amount of water soluble polymer in the aqueous phase of the water-in-oil emulsion can be any value or can range between any of the values recited above.

**[0045]** In some embodiments, the water soluble polymer in the water-in-oil emulsion is prepared by polymerizing a monomer solution that includes non-ionic monomers, cationic monomers and sulfonic acid containing monomers included at a level that provides the desired amount of water soluble polymer.

**[0046]** In some embodiments, the monomer mixture typically includes acrylamide as a non-ionic monomer. In some embodiments, the amount of non-ionic monomer can be at least about 30, in some cases at least about 33, and in other cases at least about 35 weight percent based on the weight of the monomer mixture. Without being limited by theory, it is believed that when the amount of non-ionic monomer is too low, the molecular weight of the resulting water soluble polymer may be lower than desired. In some embodiments, the amount of non-ionic monomer in the monomer mixture can be up to about 50, in some case up to about 47.5, and in other cases up to about 45 weight percent based on the weight of the monomer mixture. Without being limited by theory, it is believed that when the amount of non-ionic monomer is too high, the water soluble polymer may not carry enough ionic charge to optimally function as intended. The amount of non-ionic monomer in the monomer mixture can be any value or range between any of the values recited above.

**[0047]** In some embodiments, the non-ionic monomer is acrylamide.

**[0048]** In many embodiments, the monomer mixture includes a sulfonic acid containing monomer or its corresponding salts. In some embodiments, the sulfonic acid containing monomer is the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPSA). In some embodiments, the amount of sulfonic acid containing monomer can be at least about 5, in some cases at least about 6, and in other cases at least about 8 weight percent based on the weight of the monomer mixture. Without being limited by theory, it is believed that when the amount of sulfonic acid containing monomer is too low, the water soluble polymer may not carry enough anionic charge to optimally function as intended. In some embodiments, the amount of sulfonic acid containing monomer in the monomer mixture can be up to about 15, in some case up to about 14, and in other cases up to about 12 weight percent based on the weight of the monomer mixture. Without being limited by theory, it is believed that when the amount of sulfonic acid containing monomer is too high, the water soluble polymer may have undesirable flocculation properties when used in some embodiments. The amount of sulfonic acid containing monomer in the monomer mixture can be any value or range between any of the values recited above.

**[0049]** In many embodiments, the monomer mixture includes a cationic monomer or its corresponding salts, non-

limiting examples being chloride salts. Particular useful examples of cationic monomers include, but are not limited to, methacrylamidopropyltrimethyl ammonium chloride (MAPTAC) and acryloyloxyethyltrimethyl ammonium chloride (AETAC). In some embodiments, the amount of cationic monomer can be at least about 40, in some cases at least about 42.5, and in other cases at least about 45 weight percent based on the weight of the monomer mixture. Without being limited by theory, it is believed that when the amount of cationic monomer is too low, the water soluble polymer may not carry enough cationic charge to optimally function as intended. In some embodiments, the amount of cationic monomer in the monomer mixture can be up to about 60, in some case up to about 57.5, and in other cases up to about 55 weight percent based on the weight of the monomer mixture. Without being limited by theory, it is believed that when the amount of cationic monomer is too high, the water soluble polymer may have undesirable flocculation properties when used in the present method. The amount of cationic monomer in the monomer mixture can be any value or range between any of the values recited above.

**[0050]** Typically, the composition of the water soluble polymer will be the same or about the same as the composition of the monomer mixture.

**[0051]** Not being limited to any single theory, it is believed that the water soluble polymers described herein do not significantly decrease their hydrodynamic volume due to the presence of ions in the aqueous solution as is the case with prior art water soluble polymers.

**[0052]** The water-in-oil emulsion may, in some embodiments, be made down into a 2 wt % aqueous solution of the inverted water-in-oil emulsion. The bulk viscosity of the solution can be measured at 25° C. using a Brookfield RV instrument equipped with an appropriate spindle at 10 rpm at 25° C. (Brookfield Engineering Laboratories, Inc., Middleboro, Mass.).

**[0053]** Thus, the water soluble polymers in the dispersed aqueous phase particles of the water-in-oil emulsions described herein are, in some embodiments, able to provide a greater friction reducing effect by reducing the energy losses due to friction in high dissolved solids containing aqueous solutions. As a non-limiting example, the water soluble polymers described herein can reduce energy losses during introduction of the aqueous into a well bore due to friction between the aqueous solution in turbulent flow and the formation and/or tubular good(s) (e.g., a pipe, coiled tubing, etc.) disposed in the well bore.

**[0054]** In some embodiments, the water-in-oil emulsion containing the water soluble polymer of the present method is prepared using water-in-oil emulsion polymerization techniques. Suitable methods to effect such polymerizations are known in the art, non-limiting examples of such being disclosed in U.S. Pat. Nos. 3,284,393; 4,024,097; 4,059,552; 4,419,344; 4,713,431; 4,772,659; 4,672,090; 5,292,800; and 6,825,301, the relevant disclosures of which are incorporated herein by reference.

**[0055]** In some embodiments, the water-in-oil polymerization is carried out by mixing the surfactants with the oil phase, which contains the inert hydrophobic liquid. The aqueous phase is then prepared combining a monomer mixture with water in the desired concentration. Additionally, a chelant, such as a sodium salt of EDTA can optionally be added to the aqueous phase and the pH of the aqueous phase can be adjusted to 3.0 to 10.0, depending on the particular monomer

(s) in the monomer mixture. The aqueous phase is then added to the mixture of oil phase and surfactants. The surfactants enable the aqueous phase, which contains the monomer mixture, to be emulsified into and form discrete particles in the oil phase. Polymerization is then carried out in the presence of a free radical generating initiator.

**[0056]** Any suitable initiator can be used. Non-limiting examples of suitable initiators include diethyl 2,2'-azobisisobutyrate, dimethyl 2,2'-azobisisobutyrate, 2-methyl 2'-ethyl azobisisobutyrate, benzoyl peroxide, lauroyl peroxide, sodium persulfate, potassium persulfate, tert-butyl hydroperoxide, dimethane sulfonyl peroxide, ammonium persulfate, azobisisobutyronitrile, dimethyl 2,2'-azobis(isobutyrate) and combinations thereof.

**[0057]** In some embodiments, the amount of initiator can be from about 0.01 to 1% by weight of the monomer mixture, in some cases from 0.02% to 0.5% by weight of the monomer mixture.

**[0058]** In some embodiments, the polymerization technique may have an initiation temperature of about 25° C. and proceed approximately adiabatically. In other embodiments, the polymerization can be carried out isothermally at a temperature of about from 37° C. to about 50° C.

**[0059]** In some embodiments, the oil-in-water emulsion can include a salt. Among other things, the salt can be present to add stability to the emulsion and/or reduced viscosity of the emulsion. Examples of suitable salts, include, but are not limited to, ammonium chloride, potassium chloride, sodium chloride, ammonium sulfate, and mixtures thereof.

**[0060]** In some embodiments, the salt can be present in emulsions in an amount in the range of from about 0.5% to about 2.5% by weight of the emulsion.

**[0061]** In some embodiments, the oil-in-water emulsions can include an inhibitor. Among other things, the inhibitor can be included to prevent premature polymerization of the monomers prior to initiation of the emulsion polymerization reaction. As those of ordinary skill in the art will appreciate, with the benefit of this disclosure, the water soluble polymer may have been synthesized using an emulsion polymerization technique wherein the inhibitor acted to prevent premature polymerization. Examples of suitable inhibitors include, but are not limited to, quinones. An example of a suitable inhibitor comprises a 4-methoxyphenol (MEHQ). The inhibitor should be present in an amount sufficient to provide the desired prevention of premature polymerization. In some embodiments, the inhibitor may be present in an amount in the range of from about 0.001% to about 0.1% by weight of the emulsion.

**[0062]** The water soluble polymers described herein typically have a molecular weight sufficient to provide desired rheological properties in the aqueous ampholyte polymer solutions. In some embodiments, the water soluble polymers described herein may have a higher molecular weight in order to provide a desirable level of friction reduction. As a non-limiting example, the weight average molecular weight of the present copolymers may be in the range of from about 2,000,000 to about 20,000,000, as determined using intrinsic viscosity. Those of ordinary skill in the art will recognize that friction reducing copolymers having molecular weights outside the listed range may still provide some degree of friction reduction in an aqueous ampholyte polymer solutions.

**[0063]** As used herein, intrinsic viscosity is determined using a Ubbelohde Capillary Viscometer and solutions of the water soluble polymer in 1M NaCl solution, at 30° C., and pH

7 at 0.05 wt. %, 0.025 wt. % and 0.01 wt. % and extrapolating the measured values to zero concentration to determine the intrinsic viscosity. The molecular weight of the water soluble polymer is then determined using the Mark-Houwink equation as is known in the art.

**[0064]** Alternatively, the reduced viscosity of the water soluble polymer at 0.05 wt. % concentration is used to measure molecular size. In some embodiments, the water soluble polymer has a reduced viscosity, as determined in a Ubbelohde Capillary Viscometer at 0.05% by weight concentration of the polymer in 1M NaCl solution, at 30° C., pH 7, of from about 10 to about 40 dl/g, in some cases from 15 to about 35 dl/g, and in other cases 15 to about 30 dl/g.

**[0065]** Suitable water soluble polymers described herein can be in an acid form or in a salt form. A variety of salts can be made by neutralizing the acid form sulfonic acid containing monomer with a base, such as sodium hydroxide, potassium hydroxide, ammonium hydroxide or the like. As used herein, the term "water soluble polymer" or "ampholyte polymeric compound" is intended to include both the acid form of the water soluble copolymer and its various salts.

**[0066]** In some embodiments, the water-in-oil emulsion is added to water by inverting the emulsion to form an aqueous solution. As used herein, the terms "invert" and/or "inverting" refer to exposing the water-in-oil emulsion to conditions that cause the aqueous phase to become the continuous phase. This inversion releases the water soluble polymer into the make up water.

**[0067]** Methods of inverting water soluble polymer containing water-in-oil emulsions are known in the art and are disclosed, as a non-limiting example in U.S. Pat. No. 3,624,019.

**[0068]** In some embodiments, in order to aid the inversion, make down and dissolution of the water soluble polymer, an inverting surfactant can be included in the water-in-oil emulsion. Among other things, the inverting surfactant can facilitate the inverting of the emulsion upon addition to make up water and/or the aqueous solution described herein. As those of ordinary skill in the art will appreciate, with the benefit of this disclosure, upon addition to the aqueous solution, the water-in-oil emulsion should invert, releasing the copolymer into the aqueous solution.

**[0069]** Non-limiting examples of suitable inverting surfactants include, polyoxyethylene alkyl phenol; polyoxyethylene (10 mole) cetyl ether; polyoxyethylene alkyl-aryl ether; quaternary ammonium derivatives; potassium oleate; N-cetyl-N-ethyl morpholinium ethosulfate; sodium lauryl sulfate; condensation products of higher fatty alcohols with ethylene oxide, such as the reaction product of oleyl alcohol with 10 ethylene oxide units; condensation products of alkylphenols and ethylene oxide, such as the reaction products of isooctylphenol with 12 ethylene oxide units; condensation products of higher fatty acid amines with five, or more, ethylene oxide units; ethylene oxide condensation products of polyhydric alcohol partial higher fatty esters, and their inner anhydrides (e.g., mannitol anhydride, and sorbitol-anhydride).

**[0070]** In some embodiments, the inverting surfactants can include ethoxylated nonyl phenols, ethoxylated nonyl phenol formaldehyde resins, ethoxylated alcohols, nonionic surfactants with an HLB of from 12 to 14, and mixtures thereof.

**[0071]** A specific non-limiting example of a suitable inverting surfactant includes an ethoxylated C<sub>12</sub>-C<sub>16</sub> alcohol. The inverting surfactant can be present in an amount sufficient to

provide the desired inversion of the emulsion upon contact with the water in the aqueous solution. In some embodiments, the inverting surfactant can be present in an amount in the range of from about 1% to about 5%, in some cases from about 1.5% to about 3.5% by weight of the water-in-oil emulsion.

**[0072]** In some embodiments, the inverting surfactants are added to the water-in-oil emulsion after the polymerization is completed.

**[0073]** In some embodiments, a batch method can be used to make down the water-in-oil emulsion. In this embodiment, the water soluble polymer containing water-in-oil emulsion and water are delivered to a common mixing tank. Once in the tank, the solution is beat or mixed for a specific length of time in order to impart energy thereto. After mixing, the resulting solution must age to allow enough time for the molecules to unwind. In some instances, the this period of time is significantly reduced when using the water soluble polymers described herein.

**[0074]** In some embodiments, continuous in-line mixers as well as in-line static mixers can be used to combine the water soluble polymer containing water-in-oil emulsion and water. Non-limiting examples of suitable mixers utilized for mixing and feeding are disclosed in U.S. Pat. Nos. 4,522,502; 4,642,222; 4,747,691; and 5,470,150. Non-limiting examples of suitable static mixers can be found in U.S. Pat. Nos. 4,051,065 and 3,067,987.

**[0075]** In some embodiments, once the water soluble polymer containing water-in-oil emulsion is made down into water, any other additives are added to the aqueous ampholyte polymer solutions.

**[0076]** In some embodiments, the aqueous solution containing water soluble polymers described herein can be included in any aqueous treatment fluid used in subterranean treatments to reduce friction. Such subterranean treatments may include, but are not limited to, drilling operations, stimulation treatments (e.g., fracturing treatments, acidizing treatments, fracture acidizing treatments), and completion operations. Those of ordinary skill in the art, with the benefit of this disclosure, will be able to recognize a suitable subterranean treatment where friction reduction may be desired.

**[0077]** In some embodiments, the water used in the aqueous ampholyte polymer solutions described herein can be freshwater, saltwater (e.g., water containing one or more salts dissolved therein), brine (e.g., produced from subterranean formations), seawater, pit water, pond water—or—the like, or combinations thereof. Generally, the water used may be from any source, provided that it does not contain an excess of compounds that may adversely affect other components in the aqueous ampholyte polymer solution.

**[0078]** In some embodiments, the water soluble polymers described herein should be included in the aqueous ampholyte polymer solution in an amount sufficient to provide the desired reduction of friction. In some embodiments, a water soluble polymer described herein may be present in an amount that is at least about 0.0025%, in some cases at least about 0.003%, in other cases at least about 0.0035% and in some instances at least about 0.05% by weight of the aqueous solution and can be up to about 4%, in some cases up to about 3%, in other cases up to about 2%, in some instances up to about 1%, in other instances up to about 0.02%, in some situations up to less than about 0.1%, in other situations, up to about 0.09%, and in specific situations, up to about 0.08% by weight of the aqueous solution. The amount of the water

soluble polymers included in the aqueous solution can be any value or range between any of the values recited above.

**[0079]** In some embodiments, the water soluble polymer described herein can be present in aqueous solution in an amount in the range of from about 0.0025% to about 0.025%, in some cases in the range of from about 0.0025% to less than about 0.01%, in other cases in the range of from about 0.0025% to about 0.009%, and in some situations in the range of from about 0.0025% to about 0.008%, by weight of the aqueous solution.

**[0080]** In some embodiments, the water-in-oil emulsions described herein are used in the aqueous ampholyte polymer solution in an amount of at least about 0.1 gallons of water-in-oil emulsion per thousand gallons of aqueous solution (gpt), in some cases at least about 0.15 gpt, and in other cases at least about 0.2 gpt and can be up to about 3 gpt, in some cases up to about 2.5 gpt, in other cases up to about 2.0 gpt, in some instances up to about 1.5 gpt, and in other instances up to about 1.5 gpt. The amount of water-in-oil emulsion used in the aqueous solution can be any value or range between any of the values recited above.

**[0081]** In some embodiments, the aqueous ampholyte polymer solution contains 100,000 to 300,000 ppm of total dissolved solids. In some embodiments, the total dissolved solids include sodium chloride. In some embodiments, the dissolved solids include 30 to 39 weight percent sodium, 0 to 9 weight percent calcium, 0 to 3 weight percent magnesium and 58 to 62 weight percent chloride.

**[0082]** In some embodiments, the aqueous ampholyte polymer solution can include total dissolved solids at a level of at least about 100,000 ppm, in some cases at least about 125,000 ppm and in other cases at least about 150,000 ppm and can be up to about 300,000 ppm, in some cases up to about 275,000 ppm and in other cases up to about 250,000 ppm. The amount of total dissolved solids in the aqueous ampholyte polymer solution can be any value or range between any of the values recited above.

**[0083]** Additional additives can, in some embodiments, be included in the aqueous ampholyte polymer solutions described herein as deemed appropriate by one of ordinary skill in the art, with the benefit of this disclosure. Examples of such additives include, but are not limited to, corrosion inhibitors, proppant particulates, acids, fluid loss control additives, and surfactants. For example, an acid may be included in the aqueous ampholyte polymer solutions.

**[0084]** In some embodiments, the aqueous ampholyte polymer solutions described herein can be used in any subterranean treatment where the reduction of friction is desired. Such subterranean treatments include, but are not limited to, drilling operations, stimulation treatments (e.g., fracturing treatments, acidizing treatments, fracture acidizing treatments), and completion operations. Those of ordinary skill in the art, with the benefit of this disclosure, will be able to recognize a suitable subterranean treatment where friction reduction may be desired.

**[0085]** In some embodiments, the present aqueous ampholyte polymer solutions demonstrate better friction reduction properties than aqueous solutions containing the same high levels of dissolved solids and water soluble polymers that contain only the same non-ionic monomers and cationic monomers, but no sulfonic acid containing monomers.

EXAMPLES

[0086] The exemplary embodiments described herein will further be described by reference to the following examples. The following examples are merely illustrative of the exemplary embodiments described herein and are not intended to be limiting. Unless otherwise indicated, all percentages are by weight.

Example 1

[0087] Two samples of an ampholyte polymeric compound comprising a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride in water were prepared at 5 gal/1,000 gal and 20 gal/1,000 gal. The samples were heated from 77° F. to 150° F. at a rate of 10° F./min and then held at a constant temperature of 150° F. As shown in FIG. 1, the viscosity at the higher concentration reduces from about 155 cP to less than about 5 cP in about 90 minutes, while at the lower concentration from about 35 cP to less than about 5 cP in about 20-25 minutes.

[0088] This example illustrates that treatment fluids comprising the aqueous ampholyte polymer solutions described herein reduce in viscosity over time (i.e., break over time), which may advantageously allow for the use of little to no breaker in the treatment fluids or in subsequent wellbore operations.

Example 2

[0089] Samples were prepared with (1) linear xanthan (known to viscosify high TDS fluids) at 60 lb/1,000 gal and (2) an ampholyte polymeric compound comprising a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride at 60 gal/1,000 gal, each in base fluids of (1) water and (2) salt water with an additional 3% KCl. The viscosity of each same in were analyzed at 77° F. and 150° F. FIG. 2 (water samples) illustrates that the ampholyte polymeric compound provides higher viscosity than linear xanthan in water. While FIG. 3 (salt water samples) illustrates that in a high TDS environment the ampholyte polymeric compound provides for a comparable viscosity to linear xanthan.

[0090] This example illustrates that treatment fluids can be viscosified to levels comparable to that of traditional viscosifying agents, including in high TDS fluids.

Example 3

[0091] Samples were prepared with individual friction reducers at a concentration of 1 gallon per thousand gallons (i.e., 0.1% by volume) in water:

- [0092] (1) a commercially available friction reducing containing partially hydrolyzed polyacrylamide;
- [0093] (2) a multi-component, cationic friction reducing agent
- [0094] (3) an ampholyte polymeric compound comprising a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride.

[0095] The salinity of the samples (measured as ppm of TDS) was then increased as the percent friction reduction (“% FR”) was analyzed by pumping the sample through a test pipe while measuring the pressure drop with a pressure transducer. The % FR is calculated based on the ratio between the mea-

sured pressure drop of the sample and the pressure drop of a fresh water control sample at the same tested flow rate and ambient temperature and pressure.

[0096] As shown in FIG. 4, the Sample 1 showed an immediate decline in the % FR with increased salinity and a dramatic drop in % FR to essentially no friction reduction from about 100,000 to about 150,000 ppm TDS. Samples 2 and 3 showed similar performance over the salinity range tested with only about a 5%-10% variations in the % FR from 0 ppm to about 250,000 ppm TDS.

[0097] This example demonstrates that the one-component friction reducing agent of an ampholyte polymeric compound outperforms other polymeric friction reducing agents with increased TDS and provides comparable performance to the more complex friction reducing agents tend to be expensive and complicated to implement.

Example 4

[0098] Samples of an ampholyte polymeric compound comprising a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride in water were analyzed for degradation rates by analyzing the viscosity of the fluid over time at various temperatures:

- [0099] (1) room temperature,
- [0100] (2) ramp to 150° F., and
- [0101] (3) ramp to 190° F.

[0102] As shown in FIG. 5, the viscosity of the room temperature sample decreased from about 4.75 cP to about 1 cP over about 6 hours while the 150° F. sample decreased from about 5 cP to about 0.4 cP over about 25 minutes and the 190° F. sample decreased from about 5 cP to about 0.4 cP over about 15 minutes. Reduction in viscosity to such levels indicates that the polymer is partially hydrolyzed and contracted. As shown, the hydrolysis is temperature dependent indicating that in some instances the native temperature of the subterranean formation may be such that an ampholyte polymeric compound may be capable of breaking with minimal to no additional breaker.

Example 5

[0103] Samples were prepared with (1) partially hydrolyzed polyacrylamide in water (2) an ampholyte polymeric compound comprising a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride in water. The concentration of each of the polymers was at infinite dilution, which is a term known in the art that one of ordinary skill in the art can determine. The intrinsic viscosity of the samples were measured over about 75 hours. As illustrated in FIG. 6, the ampholyte polymeric compound sample reduced in intrinsic viscosity from about 95 dL/g to about 5 dL/g, while the polyacrylamide sample had a relatively steady intrinsic viscosity of about 100 dL/g over the 75 hour time frame. This demonstrates that the aqueous ampholyte polymer solutions may be capable of breaking over time without the use of chemical breakers due, at least in part, to the partial hydrolysis of the ampholyte polymeric compound (e.g., the acryloyloxy ethyl trimethyl ammonium chloride to acrylic acid).

Example 6

[0104] Samples were prepared with an ampholyte polymeric compound comprising a terpolymer of acrylamide,

2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride at 0.1 vol % in (1) water, (2) 50,000 ppm brine, and (3) 250,000 ppm brine. The samples were heated to 150° F., and the viscosity of each sample was analyzed. FIG. 7 illustrates that sample in water achieved the highest initial viscosity, while both of the brine samples achieved about 1/3 the initial viscosity as the water sample. However, over time, the higher the TDS of the sample the less reduction in the viscosity (i.e., less hydrolysis and contraction of the ampholyte polymeric compound).

#### Example 7

**[0105]** Samples were prepared with (1) 0.1 vol % polyacrylamide, (2) 0.1 vol % polyacrylamide and 1 lb/1,000 gal of a chemical breaker, and (3) 0.1 vol % of an ampholyte polymeric compound comprising a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and acryloyloxy ethyl trimethyl ammonium chloride in water. Samples were run through various core/sand pack samples to determine the regain permeability of the core/sand pack samples after treatment.

**[0106]** In the regain permeability tests, the initial permeability was measured by flowing 7% KCl through the core/sand pack sample. Then, the samples were pumped through the core/sand pack sample at a rate of five pore volumes. The treated core/sand pack sample was shut-in overnight at 150° F. The permeability was once again tested by flowing 7% KCl through the core/sand pack sample. Table 1 provides the initial permeability and percent of permeability regained.

TABLE 1

Fluid Sample	Core/Sand Pack	Initial Permeability	Regain Permeability
(2)	100 mesh sand pack	1.5 D	96%
(3)	100 mesh sand pack	1.6 D	98%
(1)	Berea core	91 mD	29%
(2)	Berea core	106 mD	83%
(3)	Berea core	77 mD	80%
(2)	Nugget	2.5 mD	54%
(3)	Nugget	1.8 mD	61%

**[0107]** This example demonstrates that the ampholyte polymeric compound, with no additional chemical breaker, provides for similar or better regain in permeability to a traditional friction reducer with a chemical breaker.

**[0108]** Therefore, the exemplary embodiments described herein are 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 exemplary embodiments described herein exemplary embodiments described herein 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, combined, or modified and all such variations are considered within the scope and spirit of the exemplary embodiments described herein. The exemplary embodiments described herein illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. 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 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.

#### Example 8

**[0109]** Preparation of water-in-oil emulsion polymers, percentages expressed as weight percent of the water-in-oil emulsion composition.

**[0110]** The water-in-oil emulsion composition were prepared by combining softened water, acrylamide, cationic monomer, sulfonic acid containing monomer (as detailed in the table below), EDTA and 25% sodium hydroxide (to pH of 6.5) and stirring until uniform to form the aqueous phase (about 77.5%). The oil phase (about 21.5%) was made by combining an aliphatic hydrocarbon liquid (about 20%) with surfactants (ethoxylated amine (about 1.1%), sorbitan monooleate (about 0.15%), and polyoxyalkylene sorbitan monooleate (about 0.25%) with mixing. The aqueous phase was added to the oil phase with mixing to form a dispersion of the aqueous phase dispersed in the continuous oil phase. The dispersion was heated to an initiation temperature while sparging with nitrogen and sodium metabisulfite and an oil soluble peroxide initiator was added to the dispersion to initiate polymerization. Typically, the oil phase was added to a glass resin kettle and once agitation was begun, the aqueous phase was added to the resin kettle. The resulting dispersion was sparged with nitrogen for 30 minutes while the temperature was equilibrated to 25° C., at which time 37 microliters of peroxide was added to the stirring dispersion and 0.075% sodium metabisulfite (SMBS) solution was fed to the dispersion at a rate of 0.1 milliliters per minute. The polymerization temperature was controlled between 38° and 42° C. for approximately 90 minutes. Residual monomers were scavenged by feeding 25% sodium metabisulfite (SMBS) solution at a rate of 1.0 milliliters per minute. An inverting surfactant (about 1%) was blended into the water-in-oil polymer emulsion to aid in make-down on use and the dispersion was subsequently cooled to room temperature. The resulting water-in-oil emulsion contained about 30% of water soluble polymer.

Sample	Acrylamide (%)	Cationic Monomer (%)	Acid Functional Monomer (%)
A	40	50 (AETAC)	10 (NaAMPSA)
	Comparative Prior Art Examples		
B	40	60 (AETAC)	—
C	70	—	30 (acrylic acid)

Friction Flow Loop Testing

[0111] A friction flow loop was constructed from 5/16" inner diameter stainless steel tubing, approximately 30 feet in overall length. Test solutions were pumped out of the bottom of a tapered 5 gallon reservoir. The solution flowed through the tubing and was returned back into the reservoir. The flow is achieved using a plunger pump equipped with a variable speed drive. Pressure is measured from two inline gages, with the last gage located approximately 2 ft from the discharge back into reservoir.

[0112] Four gallons of brine solution (weight percent of salt indicated below) was prepared in the sample reservoir and the pump is started and set to deliver a flow rate of 5-10 gal/min. The salt solution is recirculated until the temperature equilibrates at 25° C. and a stabilized pressure differential is achieved. This pressure is recorded as the "initial pressure" of the brine solution. The test amount of neat water-in-oil emulsion polymer is quickly injected with a syringe into the sample reservoir containing the brine solution and a timer was started. The dose was recorded as gallons of water-in-oil emulsion per thousand gallons of brine solution (gpt). The pressure was recorded at 30 seconds, 1 min, 2 min and 3 min respectively. The pressure drop was calculated at each time interval comparing it to the initial pressure differential reading of the high dissolved solids solution. The percentage friction reduction was determined as described in U.S. Pat. No. 7,004,254 at col. 9, line 36 to col. 10, line 43. The results are shown in the table below, dose is the amount of water-in-oil emulsion used as gallons per thousand gallons of brine solution.

Run No.	Emulsion Sample	Dissolved Solids (ppm NaCl)	Dose (gpt)	Friction Reduction (%)			
				30 sec.	1 min.	2 min.	3 min.
1	A	150,000	1	46.8	61.6	72.2	74.7
Comparative Prior Art Examples							
2	B	150,000	1	34.1	53	69.4	72.8
3	C	150,000	1	10.2	15.7	21.5	27.8

[0113] The data show that the inventive aqueous ampholyte polymer solutions demonstrates better friction reduction properties than aqueous polymer solutions containing prior art copolymers.

[0114] Thus, the water-in-oil polymer emulsion polymers described herein are able to provide significantly better friction reduction performance in high dissolved solids solutions compared to the prior art water-in-oil polymer emulsion polymers.

Example 9

[0115] A water-in-oil emulsion polymer (Sample D) was prepared as described in Example 8 having 24.6% active polymer having a composition of 40 wt. % acrylamide, 10 wt. % NaAMPSA, and 50 wt. % AETAC. Samples B and C were used as comparative examples again. The water-in-oil emulsion polymer was tested in a friction flow loop as described in Example 8, where the water contained dissolved solids having the following ratios: 29.4% Na, 7.4% Ca, 1.2% Mg, and 62% Cl at the total dissolved solids level indicated.

Emulsion Sample	Dissolved Solids (ppm)	Dose (gpt)	Friction Reduction (%)				
			30 sec.	1 min.	2 min.	3 min.	
D	183,000	1	64	70.1	71.5	71	
D	183,000	1.25	65.9	71.9	72.8	72.8	
D	218,000	1	63.2	69.5	69.5	68.6	
D	218,000	1.25	67.3	69.5	69.5	68.6	
D	256,000	1	57.3	64	64	67.1	
D	256,000	1.25	68	70.2	69.8	69.8	
Comparative							
B	183,000	1	52.7	54.6	55.6	56.7	
C	183,000	1	10.0	14.2	15.8	19.2	
B	183,000	1.25	54.8	57.2	57.1	57.4	
C	183,000	1.25	12.0	16.7	19.8	20.6	
B	256,000	1	48.4	52.1	52.1	53.1	
C	256,000	1	8.0	9.2	10.3	11.1	
B	256,000	1.25	45.4	56.8	56.5	57.8	
C	256,000	1.25	7.8	8.5	10.5	10.9	

[0116] The data show that the inventive aqueous ampholyte polymer solutions demonstrates better friction reduction properties than aqueous polymer solutions containing prior art copolymers.

[0117] Thus, the water-in-oil polymer emulsion polymers described herein are able to provide significantly better friction reduction performance in high dissolved solids solutions compared to the prior art water-in-oil polymer emulsion polymers.

[0118] The exemplary embodiments have been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the exemplary embodiments.

[0119] Therefore, the exemplary embodiments described herein are 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 exemplary embodiments described herein exemplary embodiments described herein 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, combined, or modified and all such variations are considered within the scope and spirit of the exemplary embodiments described herein. The exemplary embodiments described herein illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. 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 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 mean-

ing 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.

We claim:

1. An aqueous solution comprising:
  - water;
  - from 100,000 to 300,000 ppm of dissolved solids;
  - from 0.5 to 3 gallons per thousand gallons of a water-in-oil emulsion comprising an oil phase (O) and an aqueous phase (A) at an O/A ratio of from about 1:8 to about 10:1, wherein the oil phase is a continuous phase comprising an inert hydrophobic liquid;
  - wherein the aqueous phase is present as dispersed distinct particles in the oil phase and comprises water, a water soluble polymer, and surfactants;
  - wherein the water soluble polymer comprises 30 to 50 weight percent of a non-ionic monomer, 5 to 15 weight percent of a sulfonic acid containing monomer, and 40 to 60 weight percent of a cationic monomer; and
  - wherein the water soluble polymer comprises from 10 to 35 weight percent of the water-in-oil emulsion; and an inverting surfactant.
2. The aqueous solution according to claim 1, wherein the cationic monomer is methacrylamidopropyltrimethyl ammonium chloride or acryloyloxyethyltrimethyl ammonium chloride.
3. The aqueous solution according to claim 1, wherein the nonionic monomer is acrylamide.
4. The aqueous solution according to claim 1, wherein the sulfonic acid containing monomer is 2-acrylamido-2-methylpropane sulfonic acid.
5. The aqueous solution according to claim 1, wherein the dissolved solids comprise 30 to 39 weight percent sodium, 0 to 9 weight percent calcium, 0 to 3 weight percent magnesium and 58 to 62 weight percent chloride.
6. The aqueous solution according to claim 1, wherein the water soluble polymer has a molecular weight in the range of from about 7,500,000 to about 20,000,000.
7. The aqueous solution according to claim 1, wherein the water soluble polymer has a reduced viscosity, as determined in a Ubbelohde Capillary Viscometer at 0.05% by weight concentration of the polymer in 1M NaCl solution, at 30° C., pH 7, of from about 10 to about 40 dl/g.
8. The aqueous solution according to claim 1, wherein the water-in-oil emulsion comprises at least one of an inhibitor, a salt, or an inverting surfactant.
9. The aqueous solution according to claim 1, wherein the water-in-oil emulsion comprises an ammonium salt.
10. The aqueous solution according to claim 1, wherein the water-in-oil emulsion comprises 4-methoxyphenol.
11. The aqueous solution according to claim 1, wherein the inverting surfactant is one or more selected from the group consisting of polyoxyethylene alkyl phenol; polyoxyethylene (10 mole) cetyl ether; polyoxyethylene alkyl-aryl ether; N-cetyl-N-ethyl morpholinium ethosulfate; sodium lauryl sulfate; condensation products of higher fatty alcohols with ethylene oxide, condensation products of alkylphenols and ethylene oxide, condensation products of higher fatty acid

amines with five, or more, ethylene oxide units; ethylene oxide condensation products of polyhydric alcohol partial higher fatty esters, and their inner anhydrides.

12. The aqueous solution according to claim 1, wherein the inverting surfactant comprises one or more ethoxylated C<sub>12</sub>-C<sub>16</sub> alcohols.

13. The aqueous solution according to claim 1, wherein the inert hydrophobic liquid comprises a mixture of paraffinic hydrocarbons and naphthenic hydrocarbons.

14. The aqueous solution according to claim 1, wherein the surfactants comprise a tall oil fatty acid diethanol amine, a polyoxyethylene (5) sorbitan monooleate, and a sorbitan monooleate.

15. The aqueous solution according to claim 1, wherein the aqueous solution demonstrates better friction reduction properties than an aqueous solution containing the same level of dissolved solids and the same amount of a similarly prepared water soluble polymer that contains only the same non-ionic monomers and cationic monomers, but no sulfonic acid containing monomers.

16. An aqueous solution comprising:

- water;
- from 150,000 to 250,000 ppm of dissolved solids;
- from 0.5 to 3 gallons per thousand gallons of a water-in-oil emulsion comprising an oil phase (O) and an aqueous phase (A) at an O/A ratio of from about 1:8 to about 10:1, wherein the oil phase is a continuous phase comprising an inert hydrophobic liquid;
- wherein the aqueous phase is present as dispersed distinct particles in the oil phase and comprises water, a water soluble polymer, and surfactants;
- wherein the water soluble polymer comprises 35 to 45 weight percent of a non-ionic monomer, 5 to 15 weight percent of a sulfonic acid containing monomer, and 45 to 55 weight percent of a cationic monomer; and
- wherein the water soluble polymer comprises from 10 to 35 weight percent of the water-in-oil emulsion; and an inverting surfactant.

17. The aqueous solution according to claim 16, wherein the non-ionic monomer comprises acrylamide, the sulfonic acid containing monomer comprises sodium AMPSA, and the cationic monomer comprises AETAC.

18. A water-in-oil emulsion comprising an oil phase (O) and an aqueous phase (A) at an O/A ratio of from about 1:8 to about 10:1,

- wherein the oil phase is a continuous phase comprising an inert hydrophobic liquid;
- wherein the aqueous phase is present as dispersed distinct particles in the oil phase and comprises water, a water soluble polymer, and surfactants;
- wherein the water soluble polymer comprises 35 to 45 weight percent of a non-ionic monomer, 5 to 15 weight percent of a sulfonic acid containing monomer, and 45 to 55 weight percent of a cationic monomer; and
- wherein the water soluble polymer comprises from 10 to 35 weight percent of the water-in-oil emulsion; and an inverting surfactant.

19. The water-in-oil emulsion according to claim 18, wherein the non-ionic monomer comprises acrylamide, the sulfonic acid containing monomer comprises sodium AMPSA, and the cationic monomer comprises AETAC.

20. The water-in-oil emulsion according to claim 18, wherein the surfactants comprise a tall oil fatty acid diethanol amine, a polyoxyethylene (5) sorbitan monooleate, and a sorbitan monooleate; the inert hydrophobic liquid comprises a mixture of paraffinic hydrocarbons and naphthenic hydrocarbons; and the inverting surfactant comprises one or more ethoxylated C<sub>12</sub>-C<sub>16</sub> alcohols.

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