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Estados Unidos de América**5****PCT (86)**Solicitud Internacional No. PCT/GB2006/000839Fecha: 08 de marzo de 2006Publicación Internacional No. WO 2006/106287 A1Fecha: 12 de Octubre de 2006**6****Título (54)****METODOS UTILES PARA CONTROLAR PERDIDA DE FLUIDO EN TRATAMIENTOS
SUBTERRANEOS****7****Clasificación Internacional (51)** C09K 008/508

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10	Anexos:
☒	Comprobante de pago de la tasa de presentación de la solicitud por \$ 482.000.00.
☐	Comprobante de pago por reivindicación de prioridad.
☐	Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
☐	Poderes, si fuere el caso.
☐	Documento de cesión del inventor al solicitante o a su causante.
☐	Declaraciones.
☒	Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
☒	Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
☐	Copia del examen preliminar efectuado por la IPEA.
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☐	De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
☒	Otros: VER HOJA DE DOCUMENTOS ANEXOS

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FIGURA CARACTERÍSTICA

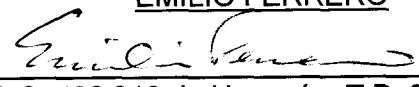
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(54) Title: METHODS USEFUL FOR CONTROLLING FLUID LOSS IN SUBTERRANEAN TREATMENTS

(57) Abstract: Provided are methods of using fluid loss control additives that comprise a water-soluble polymer with hydrophobic or hydrophilic modification. In one embodiment, a method of providing at least some degree of fluid loss control during a subterranean treatment is provided. In an example of such a method, the method may comprise providing a treatment fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble polymer with hydrophobic or hydrophilic modification; and introducing the treatment fluid into a well bore that penetrates a subterranean formation, wherein there is at least a partial reduction in fluid loss into at least a portion of the subterranean formation from the treatment fluid and/or another aqueous fluid introduced into well bore subsequent to the treatment fluid.

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METHODS USEFUL FOR CONTROLLING FLUID LOSS IN SUBTERRANEAN TREATMENTS

BACKGROUND

The present invention relates to subterranean treatments and, more particularly, to using fluid loss control additives that comprise a water-soluble polymer with hydrophobic or hydrophilic modification.

A problem often encountered during subterranean treatments is the undesired loss or leak off of fluid into the formation. This undesired loss or leak off is commonly referred to as "fluid loss." Such treatments include, but are not limited to, drilling operations, cleanup operations, workover operations, completion operations, stimulation treatments (*e.g.*, fracturing, acidizing), and sand control treatments (*e.g.*, gravel packing). In fracturing treatments, fluid loss into the formation may result in a reduction in fluid efficiency, such that the fracturing fluid cannot propagate the fracture as desired. As used herein, the term "treatment," or "treating," refers to any subterranean treatment 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 or any particular component thereof.

Fluid loss into the formation may result from a number of downhole conditions, such as high-formation permeability, overbalance pressures, perforated or open-hole intervals in the well bore, and large differential pressures associated with differential segregation in wells completed in a multilayer reservoir. In some instances, the fluid loss may be into a low-pressure portion of the formation due to overbalance pressures, for example, where a well is completed in a multilayer reservoir.

Traditional methods of combating fluid loss may involve mechanical or chemical isolation of the portions of the subterranean formation into which fluid loss occurs. However, in certain subterranean treatments (*e.g.*, workover operations), the mechanical completion itself may not allow for such isolation to occur. In some instances, the use of low-density fluids, such as hydrocarbon-based fluids or foamed fluids, may be used to combat fluid loss into the formation. However, in some instances, well conditions may not allow for the use of hydrocarbon-based fluids, for instance, due to the hydrostatic pressures associated with the hydrocarbon-based fluids. Furthermore, the use of foamed fluids may add undesired

expense and complexity to the well bore cleanup operation, as well as additional safety considerations.

In other instances, to prevent fluid loss from occurring, fluid loss control additives commonly may be included in the treatment fluids. Examples of commonly used fluid loss control additives include, but are not limited to, gelling agents, such as hydroxyethylcellulose and xanthan. Additional fluid loss control may be provided by crosslinking the gelling agent or by including fluid loss control materials, such as sized solids (e.g., calcium carbonate), silica particles, oil-soluble resins, and degradable particles, in the treatment fluids. The fluid loss control materials may be used in combination with or separately from the conventional fluid loss control additives. These conventional methods commonly work at the well bore and/or formation face and if they invade the reservoir, formation damage may occur. Additionally, the use of crosslinked fluids may impact fracture geometry, for example, creating wider, shorter fractures. Further, the crosslinked fluids may form a filter cake, which may be detrimental to the production of reservoir fluids.

Chemical fluid loss control pills also may be used to combat fluid loss. Conventional chemical fluid loss control pills may be characterized as either solids-containing pills or solids-free pills. Examples of solids-containing pills include sized-salt pills and sized-carbonate pills. These solids-containing pills often are not optimized for the particular downhole hardware and conditions that may be encountered. For instance, the particle sizes of the solids may not be optimized for a particular application and, as a result, may increase the risk of invasion into the interior of the formation matrix, which may greatly increase the difficulty of removal by subsequent remedial treatments. Additionally, high-solids loading in the pills, in conjunction with the large volumes of these pills needed to control fluid losses, may greatly increase the complexity of subsequent cleanup. Furthermore, high loading of starches and biopolymers in the sized salt pills may add to the difficulty of cleanup either by flow back or remedial treatments. Solids-free fluid loss control pills commonly comprise hydrated polymer gels that may not be effective without some invasion into the formation matrix. These pills typically require large volumes to control fluid loss and remedial treatments to remove.

Once fluid loss control is no longer required, for example, after completing a treatment, remedial treatments may be required to remove the previously placed pills, *inter alia*, so that the wells may be placed into production. For example, a chemical breaker, such

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as an acid, oxidizer, or enzyme may be used to either dissolve the solids or reduce the viscosity of the pill. In many instances, however, use of a chemical breaker to remove the pill from inside the well bore and/or the formation matrix may be either ineffective or not a viable economic option. Furthermore, the chemical breakers may be corrosive to downhole tools. Additionally, as the chemical breakers leak off into the formation, they may carry undissolved fines that may plug and/or damage the formation or may produce undesirable reactions with the formation.

SUMMARY

The present invention relates to subterranean treatments and, more particularly, to using fluid loss control additives that comprise a water-soluble polymer with hydrophobic or hydrophilic modification.

An embodiment of the present invention provides a method of providing at least some degree of fluid loss control during a subterranean treatment. In an example of such a method, the method may comprise providing a treatment fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble polymer with hydrophobic or hydrophilic modification; and introducing the treatment fluid into a well bore that penetrates a subterranean formation, wherein there is at least a partial reduction in fluid loss into at least a portion of the subterranean formation from the treatment fluid and/or another aqueous fluid introduced into the well bore subsequent to the treatment fluid.

Another embodiment of the present invention provides a method of providing at least some degree of fluid loss control during a fracturing treatment. In an example of such a method, the method may comprise providing a fracturing fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble polymer with hydrophobic or hydrophilic modification; and contacting a subterranean formation with the fracturing fluid at a pressure sufficient to create or enhance one or more fractures in the subterranean formation, wherein there is at least a partial reduction in fluid loss from the fracturing fluid into at least a portion of the subterranean formation.

Another embodiment of the present invention provides a method of providing at least some degree of fluid loss control during a subterranean treatment. In an

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example of such a method, the method may comprise providing a treatment fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble hydrophobically modified polymer, wherein the hydrophobically modified polymer comprises an amino methacrylate/alkyl amino methacrylate copolymer; and introducing the treatment fluid into a well bore that penetrates a subterranean formation, wherein there is at least a partial reduction in fluid loss into at least a portion of the subterranean formation from the treatment fluid and/or another aqueous fluid introduced into well bore subsequent to the treatment fluid.

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

DRAWINGS

A more complete understanding of the present disclosure and advantages thereof may be acquired by referring to the following description taken in conjunction with the accompanying drawings, wherein:

Figure 1 is a plot of fluid loss volume per time for a dynamic fluid loss test performed using a round cell containing a H.P. Berea sandstone core and various sample fluids.

Figure 2 is a plot of fluid loss volume per time for a dynamic fluid loss test performed using a round cell containing a L.P. Berea sandstone core and various sample fluids.

Figure 3 is a plot of fluid loss volume per time for a dynamic fluid loss test performed using a round cell containing an Ohio sandstone core and various sample fluids.

Figure 4 is a plot of fluid loss volume per time for a dynamic fluid loss test performed using a round cell containing a H.P. Berea sandstone core and various sample fluids.

Figure 5 is a plot of fluid loss volume per time for a dynamic fluid loss test performed using a round cell containing a L.P. Berea sandstone core and various sample fluids.

Figure 6 is a plot of fluid loss volume per time for a dynamic fluid loss test performed using a round cell containing an Ohio sandstone core and various sample fluids.

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While the present invention is susceptible to various modifications and alternative forms, specific exemplary embodiments thereof have been shown by way of example in the drawings and are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit or define the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims. The figures should in no way be used to limit the meaning of the claim terms.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention relates to subterranean treatments and, more particularly, to using fluid loss control additives that comprise a water-soluble polymer with hydrophobic or hydrophilic modification. As used herein, "water-soluble" refers to at least 0.01 weight percent soluble in distilled water. As used herein, the phrase "hydrophobically modified," or "hydrophobic modification," refers to the incorporation into the hydrophilic polymer structure of hydrophobic groups, wherein the alkyl chain length is from about 4 to about 22 carbons. As used herein, the phrase "hydrophilically modified," or "hydrophilic modification," refers to the incorporation into the hydrophilic polymer structure of hydrophilic groups, such as to introduce branching or to increase the degree of branching in the hydrophilic polymer. The methods and compositions of the present invention may be utilized in horizontal, vertical, inclined, or otherwise formed portions of wells.

The treatment fluids of the present invention generally comprise an aqueous liquid and a fluid loss control additive that comprises a water-soluble polymer with hydrophobic or hydrophilic modification. A variety of additional additives suitable for use in the chosen treatment may be included in the treatment fluids as desired. The aqueous liquid of the treatment fluids of the present invention may include freshwater, saltwater, brine (*e.g.*, saturated saltwater), or seawater. Generally, the aqueous liquid may be from any source, provided that it does not contain components that may adversely affect other components in the treatment fluid.

Generally, the fluid loss control additives used in the treatment fluids of the present invention comprise a water-soluble polymer with hydrophobic or hydrophilic modification. A water-soluble polymer with hydrophobic modification is referred to as hydrophobically modified. A water-soluble polymer with hydrophilic modification is referred

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to as hydrophilically modified. Among other things the fluid loss control additives should reduce fluid loss from the treatment fluid or any other aqueous fluids subsequently introduced into the well bore. It is believed that after leak off into the porosity of the subterranean formation, the water-soluble polymer should attach to surfaces within the porosity of the subterranean formation, thereby reducing the permeability of the subterranean formation to aqueous fluids without substantially changing its permeability to hydrocarbons.

The hydrophobically modified polymers useful in the present invention typically have molecular weights in the range of from about 100,000 to about 10,000,000. While these hydrophobically modified polymers have hydrophobic groups incorporated into the hydrophilic polymer structure, they should remain water-soluble. In some embodiments, a mole ratio of a hydrophilic monomer to the hydrophobic compound in the hydrophobically modified polymer is in the range of from about 99.98:0.02 to about 90:10, wherein the hydrophilic monomer is a calculated amount present in the hydrophilic polymer. In certain embodiments, the hydrophobically modified polymers may comprise a polymer backbone that comprises polar heteroatoms. Generally, the polar heteroatoms present within the polymer backbone of the hydrophobically modified polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous.

The hydrophobically modified polymers may be synthesized utilizing any suitable method. In one example, the hydrophobically modified polymers may be a reaction product of a hydrophilic polymer and a hydrophobic compound. In another example, the hydrophobically modified polymers may be prepared from a polymerization reaction comprising a hydrophilic monomer and a hydrophobically modified hydrophilic monomer. Those of ordinary skill in the art, with the benefit of this disclosure, will be able to determine other suitable methods for the synthesis of suitable hydrophobically modified polymers.

In certain embodiments, suitable hydrophobically modified polymers may be synthesized by the hydrophobic modification of a hydrophilic polymer. The hydrophilic polymers suitable for forming the hydrophobically modified polymers used in the present invention should be capable of reacting with hydrophobic compounds. Suitable hydrophilic polymers include, homo-, co-, or terpolymers such as, but not limited to, polyacrylamides, polyvinylamines, poly(vinylamines/vinyl alcohols), alkyl acrylate polymers in general, and derivatives thereof. Additional examples of alkyl acrylate polymers include, but are not limited to, polydimethylaminoethyl methacrylate, polydimethylaminopropyl methacrylamide,

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poly(acrylamide/dimethylaminoethyl methacrylate), poly(methacrylic acid/dimethylaminoethyl methacrylate), poly(2-acrylamido-2-methyl propane sulfonic acid/dimethylaminoethyl methacrylate), poly(acrylamide/dimethylaminopropyl methacrylamide), poly (acrylic acid/dimethylaminopropyl methacrylamide), and poly(methacrylic acid/dimethylaminopropyl methacrylamide). In certain embodiments, the hydrophilic polymers comprise a polymer backbone and reactive amino groups in the polymer backbone or as pendant groups, the reactive amino groups capable of reacting with hydrophobic compounds. In some embodiments, the hydrophilic polymers comprise dialkyl amino pendant groups. In some embodiments, the hydrophilic polymers comprise a dimethyl amino pendant group and a monomer comprising dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide. In certain embodiments of the present invention, the hydrophilic polymers comprise a polymer backbone that comprises polar heteroatoms, wherein the polar heteroatoms present within the polymer backbone of the hydrophilic polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous. Suitable hydrophilic polymers that comprise polar heteroatoms within the polymer backbone include homo-, co-, or terpolymers, such as, but not limited to, celluloses, chitosans, polyamides, polyetheramines, polyethyleneimines, polyhydroxyetheramines, polylysines, polysulfones, gums, starches, and derivatives thereof. In one embodiment, the starch is a cationic starch. A suitable cationic starch may be formed by reacting a starch, such as corn, maize, waxy maize, potato, and tapioca, and the like, with the reaction product of epichlorohydrin and trialkylamine.

The hydrophobic compounds that are capable of reacting with the hydrophilic polymers of the present invention include, but are not limited to, alkyl halides, sulfonates, sulfates, organic acids, and organic acid derivatives. Examples of suitable organic acids and derivatives thereof include, but are not limited to, octenyl succinic acid; dodecenyl succinic acid; and anhydrides, esters, imides, and amides of octenyl succinic acid or dodecenyl succinic acid. In certain embodiments, the hydrophobic compounds may have an alkyl chain length of from about 4 to about 22 carbons. In another embodiment, the hydrophobic compounds may have an alkyl chain length of from about 7 to about 22 carbons. In another embodiment, the hydrophobic compounds may have an alkyl chain length of from about 12 to about 18 carbons. For example, where the hydrophobic compound is an alkyl halide, the reaction between the hydrophobic compound and hydrophilic polymer may result in the

B B

quaternization of at least some of the hydrophilic polymer amino groups with an alkyl halide, wherein the alkyl chain length is from about 4 to about 22 carbons.

As previously mentioned, in certain embodiments, suitable hydrophobically modified polymers also may be prepared from a polymerization reaction comprising a hydrophilic monomer and a hydrophobically modified hydrophilic monomer. Examples of suitable methods of their preparation are described in U.S. Patent Number 6,476,169, the relevant disclosure of which is incorporated herein by reference. The hydrophobically modified polymers synthesized from the polymerization reactions may have estimated molecular weights in the range of from about 100,000 to about 10,000,000 and mole ratios of the hydrophilic monomer(s) to the hydrophobically modified hydrophilic monomer(s) in the range of from about 99.98:0.02 to about 90:10.

A variety of hydrophilic monomers may be used to form the hydrophobically modified polymers useful in the present invention. Examples of suitable hydrophilic monomers include, but are not limited to acrylamide, 2-acrylamido-2-methyl propane sulfonic acid, N,N-dimethylacrylamide, vinyl pyrrolidone, dimethylaminoethyl methacrylate, acrylic acid, dimethylaminopropylmethacrylamide, vinyl amine, vinyl acetate, trimethylammoniummethyl methacrylate chloride, methacrylamide, hydroxyethyl acrylate, vinyl sulfonic acid, vinyl phosphonic acid, methacrylic acid, vinyl caprolactam, N-vinylformamide, N,N-diallylacetamide, dimethyldiallyl ammonium halide, itaconic acid, styrene sulfonic acid, methacrylamidoethyltrimethyl ammonium halide, quaternary salt derivatives of acrylamide, and quaternary salt derivatives of acrylic acid.

A variety of hydrophobically modified hydrophilic monomers also may be used to form the hydrophobically modified polymers useful in the present invention. Examples of suitable hydrophobically modified hydrophilic monomers include, but are not limited to, alkyl acrylates, alkyl methacrylates, alkyl acrylamides, alkyl methacrylamides alkyl dimethylammoniummethyl methacrylate halides, and alkyl dimethylammoniumpropyl methacrylamide halides, wherein the alkyl groups have from about 4 to about 22 carbon atoms. In another embodiment, the alkyl groups have from about 7 to about 22 carbons. In another embodiment, the alkyl groups have from about 12 to about 18 carbons. In certain embodiments, the hydrophobically modified hydrophilic monomer comprises octadecyldimethylammoniummethyl methacrylate bromide, hexadecyldimethylammoniummethyl

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methacrylate bromide, hexadecyldimethylammoniumpropyl methacrylamide bromide, 2-ethylhexyl methacrylate, or hexadecyl methacrylamide.

Suitable hydrophobically modified polymers that may be formed from the above-described reactions include, but are not limited to, acrylamide/octadecyldimethylammoniumethyl methacrylate bromide copolymer, dimethylaminoethyl methacrylate/vinyl pyrrolidone/hexadecyldimethylammoniumethyl methacrylate bromide terpolymer, and acrylamide/2-acrylamido-2-methyl propane sulfonic acid/2-ethylhexyl methacrylate terpolymer. Another suitable hydrophobically modified polymer formed from the above-described reaction comprises an amino methacrylate/alkyl amino methacrylate copolymer. A suitable dimethylaminoethyl methacrylate/alkyl-dimethylammoniumethyl methacrylate copolymer is a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniumethyl methacrylate copolymer. As previously discussed, these copolymers may be formed by reactions with a variety of alkyl halides. For example, in some embodiments, the hydrophobically modified polymer may comprise a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniumethyl methacrylate bromide copolymer.

In another embodiment of the present invention, the fluid loss control additives of the present invention may comprise a water-soluble hydrophilically modified polymer. The hydrophilically modified polymers of the present invention typically have molecular weights in the range of from about 100,000 to about 10,000,000. In certain embodiments, the hydrophilically modified polymers comprise a polymer backbone that comprises polar heteroatoms. Generally, the polar heteroatoms present within the polymer backbone of the hydrophilically modified polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous.

The hydrophilically modified polymers may be synthesized utilizing any suitable method. In one example, the hydrophilically modified polymers may be a reaction product of a hydrophilic polymer and a hydrophilic compound. Those of ordinary skill in the art, with the benefit of this disclosure, will be able to determine other suitable methods for the preparation of suitable hydrophilically modified polymers.

In certain embodiments, suitable hydrophilically modified polymers may be formed by additional hydrophilic modification, for example, to introduce branching or to increase the degree of branching, of a hydrophilic polymer. The hydrophilic polymers

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suitable for forming the hydrophilically modified polymers used in the present invention should be capable of reacting with hydrophilic compounds. In certain embodiments, suitable hydrophilic polymers include, homo-, co-, or terpolymers, such as, but not limited to, polyacrylamides, polyvinylamines, poly(vinylamines/vinyl alcohols), and alkyl acrylate polymers in general. Additional examples of alkyl acrylate polymers include, but are not limited to, polydimethylaminoethyl methacrylate, polydimethylaminopropyl methacrylamide, poly(acrylamide/dimethylaminoethyl methacrylate), poly(methacrylic acid/dimethylaminoethyl methacrylate), poly(2-acrylamido-2-methyl propane sulfonic acid/dimethylaminoethyl methacrylate), poly(acrylamide/dimethylaminopropyl methacrylamide), poly (acrylic acid/dimethylaminopropyl methacrylamide), and poly(methacrylic acid/dimethylaminopropyl methacrylamide). In certain embodiments, the hydrophilic polymers comprise a polymer backbone and reactive amino groups in the polymer backbone or as pendant groups, the reactive amino groups capable of reacting with hydrophilic compounds. In some embodiments, the hydrophilic polymers comprise dialkyl amino pendant groups. In some embodiments, the hydrophilic polymers comprise a dimethyl amino pendant group and at least one monomer comprising dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide. In other embodiments, the hydrophilic polymers comprise a polymer backbone that comprises polar heteroatoms, wherein the polar heteroatoms present within the polymer backbone of the hydrophilic polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous. Suitable hydrophilic polymers that comprise polar heteroatoms within the polymer backbone include homo-, co-, or terpolymers, such as, but not limited to, celluloses, chitosans, polyamides, polyetheramines, polyethyleneimines, polyhydroxyetheramines, polylysines, polysulfones, gums, starches, and derivatives thereof. In one embodiment, the starch is a cationic starch. A suitable cationic starch may be formed by reacting a starch, such as corn, maize, waxy maize, potato, tapioca, and the like, with the reaction product of epichlorohydrin and trialkylamine.

The hydrophilic compounds suitable for reaction with the hydrophilic polymers include polyethers that comprise halogens, sulfonates, sulfates, organic acids, and organic acid derivatives. Examples of suitable polyethers include, but are not limited to, polyethylene oxides, polypropylene oxides, and polybutylene oxides, and copolymers, terpolymers, and mixtures thereof. In some embodiments, the polyether comprises an epichlorohydrin-terminated polyethylene oxide methyl ether.

The hydrophilically modified polymers formed from the reaction of a hydrophilic polymer with a hydrophilic compound may have estimated molecular weights in the range of from about 100,000 to about 10,000,000 and may have weight ratios of the hydrophilic polymers to the polyethers in the range of from about 1:1 to about 10:1. Suitable hydrophilically modified polymers having molecular weights and weight ratios in the ranges set forth above include, but are not limited to, the reaction product of polydimethylaminoethyl methacrylate and epichlorohydrin-terminated polyethyleneoxide methyl ether; the reaction product of polydimethylaminopropyl methacrylamide and epichlorohydrin-terminated polyethyleneoxide methyl ether; and the reaction product of poly(acrylamide/dimethylaminopropyl methacrylamide) and epichlorohydrin-terminated polyethyleneoxide methyl ether. In some embodiments, the hydrophilically modified polymer comprises the reaction product of a polydimethylaminoethyl methacrylate and epichlorohydrin-terminated polyethyleneoxide methyl ether having a weight ratio of polydimethylaminoethyl methacrylate to epichlorohydrin-terminated polyethyleneoxide methyl ether of about 3:1.

Sufficient concentrations of the fluid loss control additives of the present invention should be present in the treatment fluids of the present invention to provide the desired level of fluid loss control. In some embodiments, the fluid loss control additives should be present in the treatment fluids of the present invention in an amount in the range of from about 0.02% to about 10% by weight of the treatment fluid. In another embodiment, the fluid loss control additive should be present in the treatment fluids of the present invention in an amount in the range of from about 0.05% to about 1.0% by weight of the treatment fluid. In certain embodiments of the present invention, the fluid loss control additive may be provided in a concentrated aqueous solution prior to its combination with the other components necessary to form the treatment fluids of the present invention.

Additional additives may be added to the treatment fluids of the present invention as deemed appropriate for a particular application by one skilled in the art with the benefit of this disclosure. Examples of such additives include, but are not limited to, weighting agents, surfactants, scale inhibitors, antifoaming agents, bactericides, salts, foaming agents, acids, conventional fluid loss control additives, viscosifying agents, crosslinking agents, gel breakers, shale swelling inhibitors, combinations thereof, and the like.

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The treatment fluids of the present invention may be used in subterranean treatments where it is desirable to provide fluid loss control. Generally, the fluid loss control additives may be used at any stage of a subterranean treatment. In certain embodiments, the treatment fluid may be a drilling fluid, a fracturing fluid, a workover fluid, a well bore cleanup fluid, a gravel packing fluid, or any other suitable aqueous fluid used in subterranean treatments. In another embodiment, the treatment fluids may be a fluid loss control pill that is introduced into the well bore at any stage of the subterranean treatment. For example, the treatment fluid may be a preflush that is introduced into the well bore prior to the subterranean treatment.

Generally, the methods of the present invention comprise introducing a treatment fluid of the present invention that comprises an aqueous fluid and a fluid loss control additive that comprises a water-soluble polymer with hydrophobic or hydrophilic modification into a well bore that penetrates a subterranean formation so as to reduce fluid loss into at least a portion of the subterranean formation from the treatment fluid or another aqueous fluid introduced into the well bore subsequent to the treatment fluid. Generally, at least a portion treatment fluid should penetrate into the porosity of at least a portion of the subterranean formation at least some depth from the treated surface during normal leak off from the treatment fluid. It is believed that the water-soluble polymer present in the portion of the treatment fluid that leaked off into the formation should attach to surfaces within the porosity of the portion of the subterranean formation. The presence of the water-soluble polymers therein should reduce the permeability of treated portion of the subterranean formation to aqueous fluids without substantially changing the permeability thereof to hydrocarbons. This should reduce fluid loss into the treated portion from the treatment fluid and/or any other aqueous fluids (e.g., workover fluids, cleanup fluids, fracturing fluids, gravel packing fluids, drilling fluids, etc.) subsequently introduced into the well bore. In addition, the water-soluble polymers also may reduce subsequent problems associated with water flowing into the well bore from the treated portion of the subterranean formation. Among other things, subsequent remedial treatments should not be required to remove the water-soluble polymers prior to placing the well into production.

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

EXAMPLES

EXAMPLE 1

A fluid loss control additive useful in the present invention was prepared by mixing 47.7 grams ("g") of deionized water, 0.38 g of (n-hexadecyl) dimethylammonium ethyl methacrylate bromide, and 1.1 g of acrylamide, and sparging with nitrogen for approximately 30 minutes. Thereafter, a polymerization initiator, such as 0.0127 g of 2,2'-azo bis (2-amidinopropane) dihydrochloride was added. The resulting solution was then heated, with stirring, to 110° F and held for 18 hours to produce a highly viscous polymer solution.

EXAMPLE 2

A fluid loss control additive useful in the present invention was prepared by mixing 41.2 g of deionized water, 0.06 g of octadecyl methacrylate, 0.45 g of cocoamidopropyl betaine surfactant, and 1.26 g of acrylamide. Thereafter, a polymerization initiator, such as 0.0127 g of 2,2'-azo bis(2-amidinopropane) dihydrochloride was added. The resulting solution was then heated, with stirring, to 110° F and held for 18 hours to produce a highly viscous polymer solution.

EXAMPLE 3

A fluid loss control additive useful in the present invention was prepared as follows. First, a polymer was prepared by mixing 1,968 g of deionized water, 105 g of dimethylaminoethyl methacrylate and sparging with nitrogen for 30 minutes. Thereafter, the pH was adjusted to approximately 7.9 with sulfuric acid and a polymerization initiator, such as 0.46 g of 2,2'-azo bis(2-amidinopropane) dihydrochloride was added. The resulting solution was then heated, with stirring, to 110° F and held for 18 hours to produce poly(dimethylaminoethyl methacrylate).

The poly(dimethylaminoethyl methacrylate) was then hydrophobically modified by adding 71.0 g of it to a 250 ml round flask, followed by 15% NaOH to achieve a pH of approximately 8.9. Next, 54.6 g of water, 0.36 g of C16 alkyl (n-hexadecyl) bromide, and 0.39 g of benzylcetyldimethylammonium bromide surfactant were added to quaternize the poly(dimethylaminoethyl methacrylate) homopolymer and form a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniumethyl methacrylate copolymer. This mixture was then heated, with stirring, to 140° F and held for 24 hours to produce a highly viscous polymer solution.

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EXAMPLE 4

Fluid loss control tests were performed using a hollow Berea sandstone core with the following dimensions: 2.75-inch length, 2.5-inch outer diameter, 1-inch inner diameter. The Berea sandstone core was mounted in a cell in which fluids can be pumped through the core in two directions. In one direction, defined as the "production direction," fluid is flowed from the exterior of the core, through the core, and into the hollow interior. Fluid also may be flowed in the direction opposite the production direction so that fluid is flowed from the hollow interior of the core, through the core, and to the exterior of the core. Fluid flowing opposite the production direction represents fluid loss from a well bore into the formation. Two treatment solutions were prepared for this series of tests.

The sample treatment fluid used in Test No. 1 (comparative) was a brine containing 21% potassium chloride by weight. Test No. 1 was performed at room temperature.

The sample treatment fluid used in Tests No. 2 was prepared by adding 0.2% of a fluid loss control additive by weight to a brine containing 21% potassium chloride by weight. Accordingly, the sample treatment fluid used in Test No. 2 comprised 21% of potassium chloride by weight and 0.2% of a fluid loss control additive by weight. The fluid loss control additive was a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniummethyl methacrylate copolymer prepared as described in Example 3. Test No. 2 was performed at room temperature.

The following procedure was used for this series of tests. For each test, the core experienced a flow sequence of 1) brine, 2) oil (kerosene), 3) drilling mud (to build a filter cake), 4) sample treatment fluid, 5) oil (kerosene). The first flow step, brine, was in the production direction and prepared the core for the test. The brine used in the first flow step was a brine containing 7% potassium chloride by weight. Next, in the second flow step, the kerosene was flowed in the production direction at a constant rate until the pressure stabilized, and the initial permeability of the core was calculated. Thereafter, in the third flow step, a sample drilling mud was placed in the hollow interior of the core and pressure was applied, such that a drilling fluid filter cake was formed on the inner surface of the core. After formation of the drilling fluid filter cake, in the fourth flow step, the sample treatment fluid was placed in the inner hole, and a constant pressure of 120 psi was applied. The filtrate loss from the sample treatment fluid was then measured as a function of time. In the fifth flow

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step, kerosene was flowed in the production direction at the same rate and the final permeability of the core was calculated. For each series of tests, the initial and final permeability of the core to kerosene was essentially unchanged. Table 1 contains the data for this series of tests.

TABLE 1

Test	Polymer Concentration	Filtrate Loss (ml) at Given Time (hours)							
		1 hr	3 hrs	5 hrs	6.2 hrs	7 hrs	7.6 hrs	7.9 hrs	8.3 hrs
No. 1 @ room temperature	0	1.7	2.3	3.2	3.6	10	31	50	80
No.2 @ room temperature	2000 ppm	1.7	2.3	3.2	3.6	3.9	4.1	4.3	4.4

Accordingly, this example indicates that the above-described fluid loss control additives that comprise hydrophobically modified polymers may be useful for controlling fluid loss from a well bore into a subterranean formation.

EXAMPLE 5

Permeability reduction tests were performed using two treatment solutions and a multipressure tap Hassler sleeve containing a Brown sandstone core. The Hassler sleeve contained three pressure taps, as well as an inlet and an outlet for determining pressure, thereby dividing the core into four segments. Test No. 3 was performed at 150°F, and Test No. 4 was performed at 175°F.

The sample treatment fluid used in Test No. 3 was prepared by adding 0.6% of a fluid loss control additive by weight to a 2% by weight potassium chloride ("KCl") brine. Thus, the sample treatment fluid used in Test No. 3 comprised 2% of KCl by weight and 0.6% of a fluid loss control additive by weight. The fluid loss control additive was a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniummethyl methacrylate copolymer prepared as described in Example 3.

The sample treatment fluid used in Test No. 4 was prepared by adding 0.2% of a fluid loss control additive by weight to a 2% by weight KCl brine. Thus, the sample

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treatment fluid used in Test No. 4 comprised 2% of KCl by weight and 0.2% of a fluid loss control additive by weight. The fluid loss control additive was a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniumethyl methacrylate copolymer prepared as described in Example 3.

The following procedure was used for this series of tests. For each test, the core experienced a flow sequence of 1) brine, 2) oil (kerosene), 3) brine, 4) sample treatment fluid, 5) brine. The brine used in flow steps 1, 3, and 5 was a brine containing 7% potassium chloride by weight. The first two flow steps of brine and oil prepared the core for the test. The brine flow in step 3 was maintained until the pressure stabilized, yielding an initial permeability for the core, listed in Tables 2 and 3 below as "Initial Core Permeability." Next, 15 ml of the sample treatment fluid were flowed into the core. Next, the brine flow was reestablished until the pressure stabilized to determine the permeability of the core after treatment with the sample treatment fluid, listed in Tables 2 and 3 below as "Final Core Permeability." Initial and Final Core Permeabilities were utilized to determine a percent reduction of water permeability according to the following formula:

$$\% \text{ Reduction of Water Permeability} = (1 - \text{Final Permeability} / \text{Initial Permeability}) \times 100$$

As previously discussed, the multipressure tap Hassler Sleeve divided the core into four segments. For the above-described tests, flow steps 1, 2, 3, and 5 were from segment 1 to segment 4, and flow step 4 was from segment 4 to segment 1. The results of Test No. 3 utilizing a polymer concentration of 6,000 ppm are provided in Table No. 2 below.

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TABLE 2

	Initial Core Permeability (mDarcy)	Final Core Permeability (mDarcy)	% Reduction of Water Permeability
Segment 1	371.7	328.59	12
Segment 2	303.56	20.08	93
Segment 3	358.92	30.27	92
Segment 4	96.19	1.69	98
Total	241.46	8.36	97

The results of Test No. 4 utilizing a polymer concentration of 2,000 ppm are provided in Table No. 3 below.

TABLE 3

	Initial Core Permeability (mDarcy)	Final Core Permeability (mDarcy)	% Reduction of Water Permeability
Segment 1	2,059.79	823.65	60
Segment 2	4,372.98	1,784.29	59
Segment 3	283.76	1.74	99
Segment 4	5,281.94	4.81	100
Total	722.01	4.43	99

Accordingly, Example 5 indicates that the fluid loss control additives useful in the present invention that comprise hydrophobically modified polymers may be useful for controlling fluid loss from a well bore into a subterranean formation.

EXAMPLE 6

Permeability reduction tests were performed using two treatment solutions and a multipressure tap Hassler sleeve containing a Brown sandstone core. The Hassler sleeve

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contained three pressure taps, as well as an inlet and an outlet for determining pressure), thereby dividing the core into four segments.

The sample treatment fluid used in Test No. 5 was prepared by adding 0.2% of a fluid loss control additive by weight to a 2% by weight KCl brine. Thus, the sample treatment fluid used in Test No. 4 comprised 2% of KCl by weight and 0.2% of a fluid loss control additive by weight. The fluid loss control additive was a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniummethyl methacrylate copolymer prepared as described in Example 3. Test No. 5 was performed at 150°F.

The following procedure was used for this series of tests. For each test, the core experienced a flow sequence of 1) brine, 2) oil (kerosene), 3) sample treatment fluid, 4) oil (kerosene). The first flow step of brine prepared the core for the test. The brine used in flow step 1 was a brine containing 7% KCl by weight. The oil flow in step 2 was maintained until the pressure stabilized, yielding an initial permeability for the core, listed in Tables 2 and 3 below as "Initial Core Permeability." Next, the sample treatment fluid was flowed into the core. Next, the oil flow was reestablished until the pressure stabilized to determine the permeability of the core after treatment with the sample treatment fluid, listed in Tables 2 and 3 below as "Final Core Permeability." Initial and Final Core Permeabilities were utilized to determine a percent reduction of oil permeability according to the following formula:

$$\% \text{ Reduction of Oil Permeability} = (1 - \text{Final Permeability}/\text{Initial Permeability}) \times 100$$

As previously discussed, the multipressure tap Hassler Sleeve divided the core into four segments. For the above-described tests, flow steps Nos. 1, 2, and 4 were from segment 1 to segment 4, and flow step No. 3 was from segment 4 to segment 1. The results of Test No. 5 utilizing a polymer concentration of 2,000 ppm are provided in Table No. 4 below.

TABLE 4

	Initial Core Permeability (mDarcy)	Final Core Permeability (mDarcy)	% Reduction of Water Permeability
Total	3,571.5	4,725.25	-32

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Accordingly, this example indicates that the above-described fluid loss control additives that comprise hydrophobically modified polymers may be useful for controlling fluid loss from a well bore into a subterranean formation.

EXAMPLE 7

A fluid loss control additive useful in the present invention was prepared as follows. First, a polymer was prepared by mixing 45.0 g of dimethylaminoethyl methacrylate, 6.8 g acrylic acid, 372.0 g of water and sparging with nitrogen for 30 minutes. Thereafter, the pH was adjusted to approximately 5.3 with 5.7 mL of concentrated sulfuric acid, followed by the addition of 0.2 mL of 2-mercaptoethanol and 1.3 g of 2,2'-azo bis (2-amidinopropane) dihydrochloride. The resulting solution was then heated to 71° C, with stirring, and held for 18 hours to produce poly(dimethylaminoethyl methacrylate/acrylic acid).

The poly(dimethylaminoethyl methacrylate/acrylic acid) was then hydrophilically modified by adding 95.0 g of the polymer to a 250 mL roundbottom flask, followed by the addition of 5.7 g of a 65% solution of an epichlorohydrin-terminated polyethylene oxide methyl ether and 8.0 g of sodium chloride. Approximately 17 mL of 3% active sodium hydroxide solution was then added to reach a pH of approximately 8.2. The mixture was then heated, with stirring, to 71° C. The viscosity of the solution was monitored, and when the viscosity reached 2000 centipoise (as measured with a Brookfield LVT viscometer, #2 spindle at 12 rpm, 25° C) the reaction was terminated by removing the heat source and adding 5 mL of 17% hydrochloric acid, 2.0 g sodium chloride and 14.7 g water.

EXAMPLE 8

Dynamic fluid loss control tests were performed using four sample fluids and a round cell containing a formation core sample. High Pressure ("HP") Berea Sandstone, Low Pressure ("LP") Berea Sandstone, and Ohio Sandstone core samples were used for this series of tests.

The following procedure was used for this series of tests. The formation core samples were cut for a round core holder and placed into the core holder. The round core holder used a 1.5-inch diameter core. There was a 0.16-inch gap to allow fluid flow through the cell and across the core face for the dynamic test conditions. The round cells were heated to 140°F.

After the round cells were prepared, the sample fluid was pumped through 340 feet of 0.194-inch I.D. tubing to provide preconditioning and shear history for the fluid.

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The shear rate was approximately 440 sec^{-1} at a pump rate of 0.31 l/min. After exiting this tubing, the sample fluid was pumped into a 0.402-inch I.D. tubing section (110 feet) that was immersed in a heating bath. This simulated the lower shear rate of fluid flow in a fracture. The shear rate was about 50 sec^{-1} . For this series of test, the sample fluid was heated to 140°F as it flowed through this tubing section. After exiting this tubing section, the sample fluid was forced through the heated round cells where the dynamic fluid loss occurred. The gap for fluid flow in the round cell created the same shear rate (50 sec^{-1}) as in the previous tubing section. A 1,000-psi pressure differential drives fluid loss through the formation core sample. The fluid loss test was continued for the desired length of time while fluid loss volumes were collected.

Sample Fluid No. 1 (comparative) was a WaterFrac™ 25 fluid system having a gelling agent concentration of 25 pounds per thousand gallons (lbs/mgal). WaterFrac™ 25 is a fluid system that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. Sample Fluid No. 1 was prepared by adding 25 lbs/mgal of WG-22™ gelling agent to a base fluid. WG-22™ is a guar-based gelling agent that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. The base fluid was water that contained 2% KCl by weight. Sample Fluid No. 1 had a pH of 8.01. The viscosity of Sample Fluid No. 1 was found to be 17 cP at 74.1°F on a Fann® Model 35 Viscometer 1/5 spring at 300 rpm.

Sample Fluid No. 2 was prepared by adding 67 gallons per thousand gallons (gal/mgal) of a fluid loss control additive to the WaterFrac™ 25 fluid system of Sample Fluid No. 1. The fluid loss control additive was a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniumethyl methacrylate copolymer prepared as described in Example 3. Next, the sample was buffered to a pH of 6.09 using BA-20™ buffering agent, which is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. The viscosity of Sample Fluid No. 2 was found to be 19.7 cP at 74.1°F on a Fann® Model 35 Viscometer 1/5 spring at 300 rpm.

Sample Fluid No. 3 (comparative) was a Delta Frac® 140 25 fluid system having a gelling agent concentration of 25 lbs/mgal. Delta Frac® 140 25 is a fluid system that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. Sample No. 2 was prepared by adding 25 lbs/mgal of WG-22™ gelling agent to a base fluid. WG-22™ is a guar-based gelling agent that is commercially available from Halliburton

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Energy Services, Inc., Duncan, Oklahoma. The base fluid was water that contained 2% KCl by weight. The base gel had a pH of 7.72. The viscosity of the base gel was found to be 16.1 cP at 72.3°F on a Fann® Model 35 Viscometer 1/5 spring at 300 rpm. Next, 2 gals/mgal of BC-2 crosslinking agent was added to the base gel. BC-2 is a borate crosslinking agent that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. Next, 0.0017 gals/mgal of N-Zyme 3™ breaking agent was added to the base gel. N-Zyme 3™ is a breaking agent that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. The gelled and crosslinked Sample Fluid No. 3 had a pH of 8.55.

Sample Fluid No. 4 was prepared by adding 67 gal/mgal of a fluid loss control additive to the Delta Frac® 140 25 fluid system of Sample Fluid No. 3. The fluid loss control additive was a dimethylaminoethyl methacrylate/hexadecyl-dimethylammoniumethyl methacrylate copolymer prepared as described in Example 3. Sample Fluid No. 4 had a pH of 8.54. The viscosity of Sample Fluid No. 4 was found to be 16.2 cP at 74.1°F on a Fann® Model 35 Viscometer 1/5 spring at 300 rpm.

Dynamic fluid loss control tests were conducted in accordance with the above procedure using the H.P. Berea sandstone core sample for both Sample Fluid No. 1 and Sample Fluid No. 2. Table 5 below lists the total fluid loss volume after 4 minutes for each sample. The results of this test are also depicted in Figure 1.

TABLE 5

H.P. BEREA SANDSTONE CORE		
Fluid	Fluid Loss Control Additive (gals/mgal)	Total Fluid Loss After 4 Minutes (ml/cm ²)
Sample Fluid No. 1 (WaterFrac™ 25 Fluid System)	0	86.76
Sample Fluid No. 2 (WaterFrac™ 25 Fluid System)	67	24.69

Dynamic fluid loss control tests were conducted in accordance with the above procedure using the L.P. Berea sandstone core samples for both Sample Fluid No. 1 and Sample Fluid No. 2. Table 6 below lists the total fluid loss volume after 1 hour for each sample. The results of this test are also depicted in Figure 2.

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TABLE 6

L.P. BERE A SANDSTONE CORE		
Fluid	Fluid Loss Control Additive (gals/mgal)	Total Fluid Loss After 1 Hour (ml/cm ²)
Sample Fluid No. 1 (WaterFrac™ 25 Fluid System)	0	39.46
Sample Fluid No. 2 (WaterFrac™ 25 Fluid System)	67	3.42

Dynamic fluid loss control tests were conducted in accordance with the above procedure using the Ohio sandstone core sample for both Sample Fluid No. 1 and Sample Fluid No. 2. Table 7 below lists the total fluid loss volume after 1 hour for each sample. The results of this test are also depicted in Figure 3.

TABLE 7

OHIO SANDSTONE CORE		
Fluid	Fluid Loss Control Additive (gals/mgal)	Total Fluid Loss After 1 Hour (ml/cm ²)
Sample Fluid No. 1 (WaterFrac™ 25 Fluid System)	0	1.25
Sample Fluid No. 2 (WaterFrac™ 25 Fluid System)	67	1.18

In addition to the above tests for Sample Fluid No. 1 and No. 2, dynamic fluid loss control tests were also conducted in accordance with the above procedure for Sample Fluid No. 3 and No. 4 on each of the formation core samples. First, the dynamic fluid loss tests were conducted using the H.P. Berea sandstone core sample. Table 8 below lists the total fluid loss volume after 1 hour for each sample. The results of this test are also depicted in Figure 4.

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TABLE 8

H.P. BEREA SANDSTONE CORE		
Fluid	Fluid Loss Control Additive (gals/mgal)	Total Fluid Loss After 1 Hour (ml/cm ²)
Sample Fluid No. 3 (Delta Frac® 140 25 Fluid System)	0	4.13
Sample Fluid No. 4 (Delta Frac® 140 25 Fluid System)	67	2.51

Dynamic fluid loss control tests were conducted in accordance with the above procedure using the L.P. Berea sandstone core samples for both Sample Fluid No. 3 and Sample Fluid No. 4. Table 9 below lists the total fluid loss volume after 1 hour for each sample. The results of this test are also depicted in Figure 5.

TABLE 9

L.P. BEREA SANDSTONE CORE		
Fluid	Fluid Loss Control Additive (gals/mgal)	Total Fluid Loss After 1 Hour (ml/cm ²)
Sample Fluid No. 3 (Delta Frac® 140 25 Fluid System)	0	1.83
Sample Fluid No. 4 (Delta Frac® 140 25 Fluid System)	67	1.16

Dynamic fluid loss control tests were conducted in accordance with the above procedure using the Ohio sandstone core sample for both Sample Fluid No. 3 and Sample Fluid No. 4. Table 10 below lists the total fluid loss volume after 1 hour for each sample. The results of this test are also depicted in Figure 6.

TABLE 10

OHIO SANDSTONE CORE		
Fluid	Fluid Loss Control Additive (gals/mgal)	Total Fluid Loss After 1 Hour (ml/cm ²)
Sample Fluid No. 1 (WaterFrac™ 25 Fluid System)	0	1.84
Sample Fluid No. 2 (WaterFrac™ 25 Fluid System)	67	1.33

Accordingly, this Example illustrates that the fluid loss control additives useful in the present invention may be suitable for providing dynamic fluid loss control in a variety of formation rock types and fluid systems.

Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims. The terms in the claims have their plain, ordinary meaning unless otherwise defined by the patentee.

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What is claimed is:

1. A method of providing at least some degree of fluid loss control during a subterranean treatment, comprising:
providing a treatment fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble polymer with hydrophobic or hydrophilic modification; and
introducing the treatment fluid into a well bore that penetrates a subterranean formation, wherein there is at least a partial reduction in fluid loss into at least a portion of the subterranean formation from the treatment fluid and/or another aqueous fluid introduced into well bore subsequent to the treatment fluid.
2. The method of claim 1 wherein the water-soluble polymer is a hydrophobically modified polymer.
3. The method of claim 2 wherein the hydrophobically modified polymer comprises an amino methacrylate/alkyl amino methacrylate copolymer.
4. The method of claim 2 wherein the hydrophobically modified polymer comprises at least one of the following: an acrylamide/octadecyldimethylammoniummethyl methacrylate bromide copolymer, a dimethylaminoethyl methacrylate/vinyl pyrrolidone/hexadecyldimethylammoniummethyl methacrylate bromide terpolymer, a acrylamide/2-acrylamido-2-methyl propane sulfonic acid/2-ethylhexyl methacrylate terpolymer, or a dimethylaminoethyl methacrylate/hexadecyldimethylammoniummethyl methacrylate bromide copolymer.
5. The method of claim 2 wherein the water-soluble hydrophobically modified polymer comprises a polymer backbone that comprises polar heteroatoms.
6. The method of claim 2 wherein the hydrophobically modified polymer is a reaction product of a hydrophobic compound and a hydrophilic polymer, or is synthesized from a polymerization reaction that comprises a hydrophilic monomer and a hydrophobically modified hydrophilic monomer.
7. The method of claim 6 wherein the hydrophilic polymer comprises a polymer backbone and a reactive amino group in the polymer backbone or as a pendant group, the reactive amino group capable of reacting with the hydrophobic compound.

8. The method of claim 6 wherein the hydrophilic polymer comprises a dialkyl amino pendant group.

9. The method of claim 6 wherein the hydrophilic polymer comprises a dimethyl amino pendant group and at least one monomer comprising dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide.

10. The method of claim 6 wherein the hydrophilic polymer comprises at least one of the following: a polyacrylamide; a polyvinylamine; a poly(vinylamine/vinyl alcohol); an alkyl acrylate polymer; a cellulose; a chitosan; a polyamide; a polyetheramine; a polyethyleneimine; a polyhydroxyetheramine; a polylysine; a polysulfone; a gum; a starch; or a derivative thereof.

11. The method of claim 6 wherein the hydrophobic compound comprises at least one of the following: an alkyl halide; a sulfonate; a sulfate; an organic acid; or an organic acid derivative.

12. The method of claim 6 wherein the hydrophilic monomer comprises at least one of the following: acrylamide; 2-acrylamido-2-methyl propane sulfonic acid; N,N-dimethylacrylamide; vinyl pyrrolidone; dimethylaminoethyl methacrylate; acrylic acid; dimethylaminopropylmethacrylamide; vinyl amine; vinyl acetate; trimethylammoniumethyl methacrylate chloride; methacrylamide; hydroxyethyl acrylate; vinyl sulfonic acid; vinyl phosphonic acid; methacrylic acid; vinyl caprolactam; N-vinylformamide; N,N-diallylacetamide; dimethyldiallyl ammonium halide; itaconic acid; styrene sulfonic acid; methacrylamidoethyltrimethyl ammonium halide; a quaternary salt derivative of acrylamide; or a quaternary salt derivative of acrylic acid.

13. The method of claim 6 wherein the hydrophobically modified hydrophilic monomer comprises at least one of the following: an alkyl acrylate; an alkyl methacrylate; an alkyl acrylamide; an alkyl methacrylamide; an alkyl dimethylammoniumethyl methacrylate halide; or an alkyl dimethylammoniumpropyl methacrylamide halide; wherein the alkyl groups have from about 4 to about 22 carbon atoms.

14. The method of claim 1 wherein the water-soluble polymer is a hydrophilically modified polymer.

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15. The method of claim 14 wherein the hydrophilically modified polymer comprises a polymer backbone that comprises polar heteroatoms.
16. The method of claim 15 wherein the hydrophilically modified polymer is a reaction product of a hydrophilic polymer and a hydrophilic compound.
17. The method of claim 15 wherein the hydrophilic polymer comprises a polymer backbone and a reactive amino group in the polymer backbone or as a pendant group, the reactive amino group capable of reacting with the hydrophobic compound.
18. The method of claim 15 wherein the hydrophilic polymer comprises at least one of the following: a polyacrylamide; a polyvinylamine; a poly(vinylamine/vinyl alcohol); an alkyl acrylate polymer; a cellulose; a chitosan; a polyamide; a polyetheramine; a polyethyleneimine; a polyhydroxyetheramine; a polylysine; a polysulfone; a gum; a starch; or a derivative thereof.
19. The method of claim 15 wherein the hydrophilic compound comprises at least one of the following: a polyether comprising a halogen; a sulfonate; a sulfate; an organic acid; or an organic acid derivative.
20. The method of claim 1 wherein at least a portion of the treatment fluid leaks of into the portion of the subterranean formation and the fluid loss control additive present in the portion of the treatment fluid reduces the permeability of the portion of the subterranean formation to aqueous fluids without substantially changing the permeability of the portion to hydrocarbons.
21. A method of providing at least some degree of fluid loss control during a fracturing treatment, comprising:
- providing a fracturing fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble polymer with hydrophobic or hydrophilic modification; and
 - contacting a subterranean formation with the fracturing fluid at a pressure sufficient to create or enhance one or more fractures in the subterranean formation, wherein there is at least a partial reduction in fluid loss from the fracturing fluid into at least a portion of the subterranean formation.

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22. The method of claim 21 wherein the water-soluble polymer is a hydrophobically modified polymer, wherein the hydrophobically modified polymer is a reaction product of a hydrophilic polymer and a hydrophobic compound, or the hydrophobically modified polymer is synthesized from a polymerization reaction that comprises a hydrophilic monomer and a hydrophobically modified hydrophilic monomer.

23. The method of claim 21 wherein the hydrophobically modified polymer comprises an amino methacrylate/alkyl amino methacrylate copolymer.

24. The method of claim 21 wherein the hydrophobically modified polymer is a reaction product of a hydrophobic compound and a hydrophilic polymer, or is synthesized from a polymerization reaction that comprises a hydrophilic monomer and a hydrophobically modified hydrophilic monomer.

25. A method of providing at least some degree of fluid loss control during a subterranean treatment, comprising:

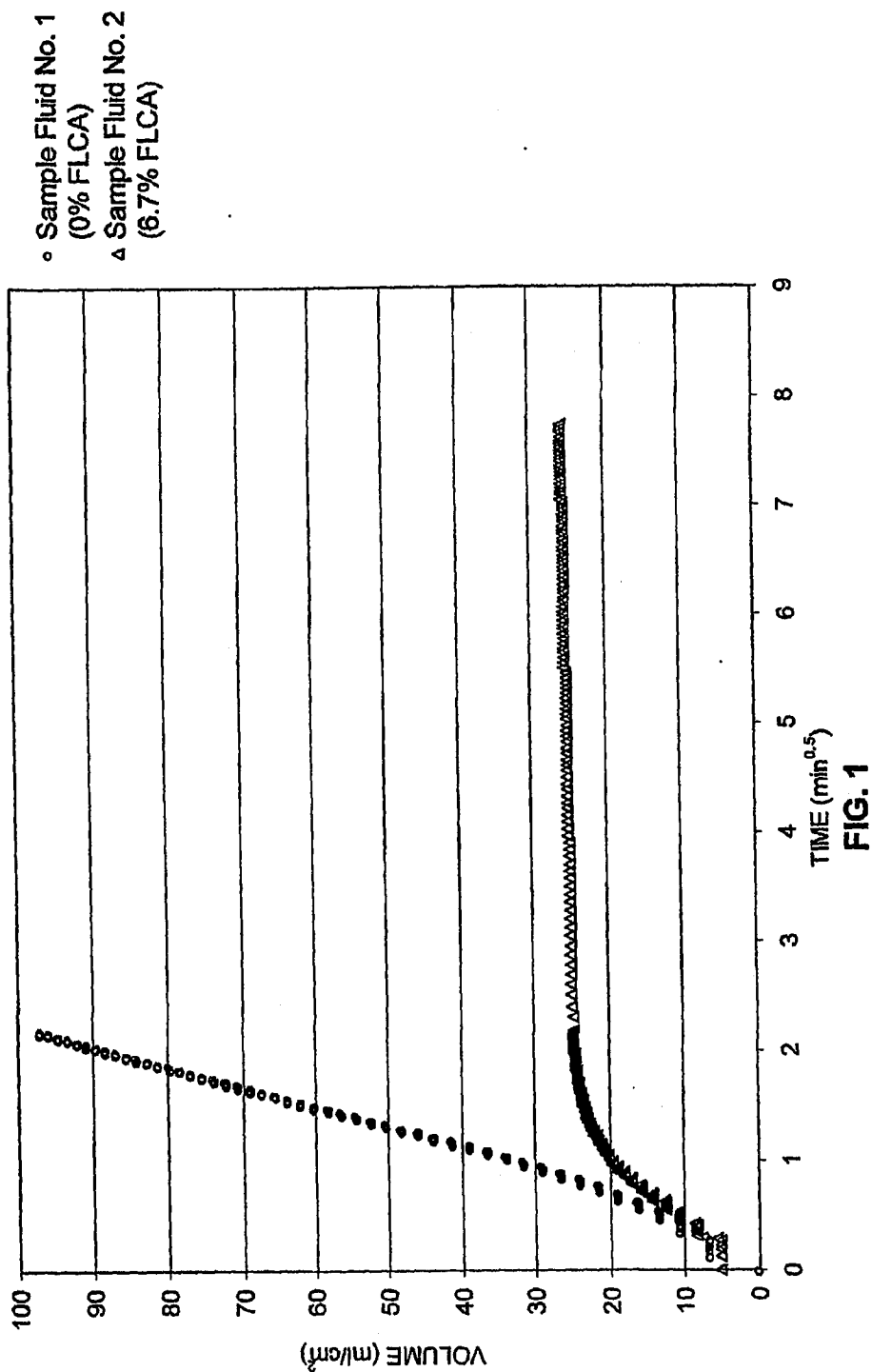
providing a treatment fluid comprising an aqueous liquid and a fluid loss control additive, the fluid loss control additive comprising a water-soluble hydrophobically modified polymer, wherein the hydrophobically modified polymer comprises an amino methacrylate/alkyl amino methacrylate copolymer; and

introducing the treatment fluid into a well bore that penetrates a subterranean formation, wherein there is at least a partial reduction in fluid loss into at least a portion of the subterranean formation from the treatment fluid and/or another aqueous fluid introduced into well bore subsequent to the treatment fluid.

26. The method of claim 25 wherein the hydrophobically modified polymer comprises a dimethylaminoethyl methacrylate/hexadecyldimethylammoniummethyl methacrylate bromide copolymer.

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MÉTODOS ÚTILES PARA CONTROLAR PÉRDIDA DE FLUIDO EN
TRATAMIENTOS SUBTERRÁNEOS

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ANTECEDENTES

La presente invención se relaciona con tratamientos subterráneos y, más particularmente, con el uso de aditivos de control de pérdida de fluido que comprenden un polímero soluble en agua con una modificación hidrófoba o

10 hidrofílica.

Un problema encontrado a menudo durante los tratamientos subterráneos es la pérdida o la chorreadura no deseada de fluido hacia la formación. Esta pérdida o chorreadura no deseada es comúnmente denominada como "pérdida de

15 fluido". Tales tratamientos incluyen, pero no están limitados a, operaciones de perforación, operaciones de limpieza, operaciones de re-acondicionamiento, operaciones de completamiento, tratamientos de estimulación (por ejemplo, fracturamiento, acidificación), y tratamientos de control de arenas (por ejemplo, relleno de cascajo). En los tratamientos de fracturamiento, la pérdida de fluido en la

20 formación puede dar como resultando una reducción en la eficiencia del fluido, de tal forma que el fluido de fracturamiento no puede propagar la fractura como se desee. Como se utiliza aquí, el término "tratamiento", o "tratar", se refiere a cualquier tratamiento subterráneo que utiliza un fluido en conjunto con una función deseada y/o para un propósito deseado. El término "tratamiento", o "tratar" no

25 implica ninguna acción particular por el fluido o cualquier componente particular de éste.

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La pérdida de fluido en la formación puede dar como resultado un número de condiciones abajo del pozo, tal como la permeabilidad de la formación alta, las presiones de sobre equilibrio, los intervalos de agujero perforado o descubierto en la perforación, y grandes presiones diferenciales asociadas con la segregación diferencial en pozos completados en un reservorio multicapa. En algunos casos, la pérdida de fluido puede estar en una porción de baja presión de la formación debido a las presiones de sobre equilibrio, por ejemplo donde un pozo es completado en un reservorio multicapa.

10 Los métodos tradicionales de combatir la pérdida de fluido pueden involucrar el aislamiento mecánico o químico de las porciones de la formación subterráneas en la cual ocurre la pérdida de fluido. Sin embargo, en ciertos tratamientos subterráneos (por ejemplo, operaciones de re-acondicionamiento), el completamiento mecánico en si mismo puede no permitir que tal aislamiento ocurra. En algunos casos, el uso de fluidos de baja densidad, tal como los fluidos basados en hidrocarburos o fluidos espumados se puede utilizar para combatir la pérdida de fluido en la formación. Sin embargo, en algunos casos, las condiciones del pozo pueden no permitir el uso de fluidos basados en hidrocarburos, por ejemplo, debido a las presiones hidrostáticas asociadas con los fluidos basados en hidrocarburo. Adicionalmente, el uso de fluidos espumados puede agregar costos y complejidad no deseados a las operaciones de limpieza de la perforación, así como también a consideraciones de seguridad adicionales.

25 En otros casos, para evitar que ocurra la pérdida de fluido, los aditivos de control de pérdida de fluido comúnmente pueden estar incluidos en los fluidos de tratamiento. Ejemplos de aditivos de control de pérdida de fluido comúnmente utilizados incluyen, pero no están limitados a, agentes gelificantes, tales como

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hidroxietilcelulosa y xantano. El control de la pérdida de fluido adicional se puede suministrar al reticular el agente gelificante o al incluir los materiales de control de pérdida de fluido, tal como los sólidos calibrados (por ejemplo, carbonato de calcio), partículas de sílice, resinas solubles en petróleo, y partículas degradables, en los fluidos de tratamiento. Los materiales de control de pérdida de fluido se pueden utilizar en combinación con o separadamente de los aditivos de control de pérdida de fluido convencionales. Estos métodos convencionales comúnmente trabajan en la perforación y/o la cara de formación y si ellos invaden el reservorio, puede ocurrir un daño en la formación. Adicionalmente, el uso de fluidos reticulados puede impactar la geometría de la fractura, por ejemplo, creando fracturas más amplias, y más cortas. Además, los fluidos reticulados pueden formar una torta de filtro, que puede estar en detrimento con la producción de los fluidos del reservorio.

Las píldoras de control de pérdida de fluido químico también se pueden utilizar para combatir la pérdida de fluido. Las píldoras de control de pérdida de fluido químicas convencionales se pueden caracterizar como píldoras que contienen sólidos o píldoras libres de sólidos. Ejemplos de píldoras que contienen sólidos incluyen píldoras de sales dimensionadas y píldoras de carbonato dimensionado. Estas píldoras que contienen sólidos a menudo no están optimizadas para el equipo en el fondo del pozo particular y las condiciones que se puedan encontrar. Por ejemplo, los tamaños de partícula de los sólidos no están optimizados para una aplicación particular y, como resultado, puede incrementar el riesgo de invasión al interior de la matriz de formación, lo cual puede incrementar mayormente la dificultad de la remoción mediante los tratamientos de remedio posteriores. Adicionalmente, la carga alta de sólidos en las píldoras, en conjunto con los grandes volúmenes de estas píldoras necesarias para controlar las

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pérdidas de fluido, pueden incrementar grandemente la complejidad de la limpieza posterior. Adicionalmente, la alta carga de los almidones y los biopolímeros en las píldoras de sal dimensionada se pueden agregar a la dificultad de la limpieza por el reflujo o los tratamientos de remedio. Las píldoras de control de pérdida de fluido libres de sólidos comúnmente comprenden geles de polímero hidratados que pueden no ser efectivos sin alguna invasión en la matriz de formación. Estas píldoras típicamente requieren grandes volúmenes para controlar la pérdida de fluido y remover los tratamientos de remedio.

10 Una vez que el control de pérdida de fluido ya no se requiera, por ejemplo, después de completar un tratamiento, los tratamientos de remedio se pueden requerir para remover las píldoras previamente colocadas, *entre otros*, de tal forma que los pozos se pueden colocar en producción. Por ejemplo, un rompedor químico, tal como un ácido, oxidante, o enzima se puede utilizar para disolver los sólidos o reducir la viscosidad de la píldora. En muchos casos, sin embargo, el uso de un rompedor químico para remover la píldora desde el interior de la perforación y/o la matriz de formación puede no ser efectivo o no ser una opción económicamente viable. Adicionalmente, los rompedores químicos pueden ser corrosivos a las herramientas abajo en el fondo del pozo. Adicionalmente, como los rompedores químicos chorrean hacia la formación, ellos pueden llevar finos no disueltos que pueden taponar y/o dañar la formación o pueden producir reacciones indeseables con la formación.

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RESUMEN

La presente invención se relaciona con tratamientos subterráneos y, más particularmente, con el uso de aditivos de control de pérdida de fluido que
5 comprende un polímero soluble en agua con modificación hidrófoba o hidrofílica.

Una modalidad de la presente invención suministra un método para suministrar por lo menos algún grado de control de pérdida de fluido durante un tratamiento subterráneo. En un ejemplo de tal método, el método puede
10 comprender suministrar un fluido de tratamiento que comprende un líquido acuoso y un aditivo de control de pérdida de fluido, el aditivo de control de pérdida de fluido comprende un polímero soluble en agua con modificación hidrófoba o hidrofílica; e introducir el fluido de tratamiento en una perforación que penetra una
15 formación subterránea, en donde existe por lo menos una reducción parcial en pérdida de fluido en por lo menos una porción de la formación subterránea proveniente del fluido de tratamiento y/u otro fluido acuoso introducido en la perforación posterior al fluido de tratamiento.

Otra modalidad de la presente invención suministra un método para
20 suministrar por lo menos algún grado de control de pérdida de fluido durante un tratamiento de fracturamiento. En un ejemplo de tal método, el método puede comprender suministrar un fluido de fracturamiento que comprende un líquido acuoso y un aditivo de control de pérdida de fluido, el aditivo de control de pérdida de fluido comprende un polímero soluble en agua con modificación hidrófoba o
25 hidrofílica; y poner en contacto una formación subterránea con el fluido de fracturamiento a una presión suficiente para crear o mejorar una o más fracturas en la formación subterránea, en donde existe por lo menos una reducción parcial

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en la pérdida de fluido proveniente del fluido de fracturamiento en por lo menos una porción de la formación subterránea.

Otra modalidad de la presente invención suministra un método para
5 suministrar por lo menos algún grado de control de pérdida de fluido durante un tratamiento subterráneo. En un ejemplo de tal método, el método puede comprender suministrar un fluido de tratamiento que comprende un líquido acuoso y un aditivo de control de pérdida de fluido, el aditivo de control de pérdida de fluido comprende un polímero modificado hidrófobamente soluble en agua, en
10 donde el polímero modificado hidrófobamente comprende un copolímero de amino metacrilato/alquil amino metacrilato; e introducir el fluido de tratamiento en una perforación que penetra una formación subterránea, en donde existe por lo menos una reducción parcial en la pérdida de fluido en por lo menos una porción de la formación subterránea proveniente del fluido de tratamiento y/u otro fluido acuosos
15 introducido en la perforación posterior al fluido de tratamiento.

Otras y adicionales características y ventajas de la presente invención serán fácilmente evidentes para aquellos expertos en la técnica luego de leer la descripción de las modalidades preferidas que siguen.

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DIBUJOS

Un entendimiento más completo de la presente descripción y las ventajas de ésta se pueden adquirir al referirse a la siguiente descripción tomada en
25 conjunto con los dibujos que la acompañan, en donde:

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La Figura 1 es una gráfica del volumen de pérdida de fluido por tiempo durante una prueba de pérdida dinámica de fluido desarrollada utilizando una celda redonda que contiene un núcleo de arenisca de Berea H.P. y varios fluidos de muestra.

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La Figura 2 es una gráfica del volumen de pérdida de fluido por tiempo durante una prueba de pérdida dinámica de fluido desarrollada utilizando una celda redonda que contiene un núcleo de arenisca de Berea L.P. y varios fluidos de muestra.

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La Figura 1 es una gráfica del volumen de pérdida de fluido por tiempo durante una prueba de pérdida dinámica de fluido desarrollada utilizando una celda redonda que contiene un núcleo de arenisca de Ohio y varios fluidos de muestra.

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La Figura 4 es una gráfica del volumen de pérdida de fluido por tiempo durante una prueba dinámica de pérdida de fluido desarrollada utilizando una celda redonda que contiene un núcleo de arenisca de Berea H.P. y varios fluidos de muestra.

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La Figura 5 es una gráfica del volumen de pérdida de fluido por tiempo durante una prueba dinámica de pérdida de fluido desarrollada utilizando una celda redonda que contiene un núcleo de arenisca de Berea L.P. y varios fluidos de muestra.

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La Figura 6 es una gráfica del volumen de pérdida de fluido por tiempo durante una prueba dinámica de pérdida de fluido desarrollada utilizando una

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celda redonda que contiene un núcleo de arenisca de Ohio y varios fluidos de muestra.

Aunque la presente invención es susceptible a varias modificaciones y formas alternativas, las modalidades de ejemplo específicas de éstas se han
5 mostrado por vía de ejemplo en los dibujos y se describen aquí en detalle. Se debe entender, sin embargo, que la descripción aquí de las modalidades específicas no pretende limitar o definir la invención a las formas particulares descritas, sino por el contrario, la intención es cubrir todas las modificaciones,
10 equivalentes, y alternativas que caen dentro del espíritu y alcance de la invención como se define en las reivindicaciones finales. Las figuras no deben ser consideradas de ninguna manera, limitantes a los términos de las reivindicaciones.

DESCRIPCIÓN DE LAS MODALIDADES PREFERIDAS

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La presente invención se relaciona con tratamientos subterráneos y, más particularmente, con el uso de aditivos de control de pérdida de fluido que comprende un polímero soluble en agua con una modificación hidrófoba o hidrofílica. Como se utiliza aquí, "soluble en agua" se refiere a por lo menos 0.01
20 por ciento en peso soluble en agua destilada. Como se utiliza aquí, la frase "hidrófobamente modificado", o "modificación hidrofóbica", se refiere a la incorporación en la estructura de polímero hidrofílica de grupos hidrófobos, en donde la longitud de la cadena de alquilo es de aproximadamente 4 a 22 carbonos. Como se utiliza aquí, la frase "hidrofílicamente modificado", o
25 "modificación hidrofílica", se refiere a la incorporación en la estructura de polímero hidrofílica de grupos hidrofílicos, tales como introducir ramificación o incrementar el grado de ramificación en el polímero hidrofílico. Los métodos y composiciones

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de la presente invención se pueden utilizar en porciones de pozos horizontales, verticales, inclinados, o formados de otra manera.

Los fluidos de tratamiento de la presente invención generalmente comprenden un líquido acuoso y un aditivo de control de pérdida de fluido que comprende un polímero soluble en agua con modificación hidrófoba o hidrofílica. Una variedad de aditivos adicionales adecuados para el uso en el tratamiento escogido se pueden incluir en los fluidos de tratamiento según se desee. El líquido acuoso de los fluidos de tratamiento de la presente invención puede incluir agua fresca, agua con sal, solución salina (por ejemplo, agua salada saturada), o agua de mar. En general, el líquido acuoso puede provenir de cualquier fuente, siempre y cuando ésta no contenga componentes que puedan afectar adversamente a otros componentes en el fluido de tratamiento.

En general, los aditivos de control de pérdida de fluido utilizados en los fluidos de tratamiento de la presente invención comprenden un polímero soluble en agua con una modificación hidrófoba o hidrofílica. Un polímero soluble en agua con una modificación hidrófoba se denomina con hidrófobamente modificado. Un polímero soluble en agua con una modificación hidrofílica se denomina como modificado hidrofílicamente. Entre otras cosas los aditivos de control de pérdida de fluido deben reducir la pérdida de fluido proveniente del fluido de tratamiento o cualquier otros fluidos acuosos posteriormente introducidos en la perforación. Se cree que después de la chorreadura en la porosidad de la formación subterránea, el polímero soluble en agua debe unirse a las superficies dentro de la porosidad de la formación subterránea, reduciendo de esta manera la permeabilidad de la formación subterránea a los fluidos acuosos sin cambiar sustancialmente su permeabilidad a los hidrocarburos.

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Los polímeros hidrófobamente modificados útiles en la presente invención típicamente tienen pesos moleculares en el rango de desde aproximadamente 100,000 a aproximadamente 10,000,000. Aunque estos polímeros hidrófobamente modificados tiene grupos hidrofóbicos incorporados en la estructura de polímero hidrofílica, ellos deben permanecer solubles en agua. En algunas modalidades, una proporción en mol de un monómero hidrofílico al compuesto hidrofobo en el polímero modificado hidrofobamente está en el rango de desde aproximadamente 99.98:0.02 a aproximadamente 90:10, en donde el monómero hidrofílico es una cantidad calculada presente en el polímero hidrofílico. En ciertas modalidades, los polímeros hidrofobamente modificados pueden comprender una estructura de polímero que comprenda heteroátomos polares. En general, los heteroátomos polares presentes dentro de la estructura del polímero de los polímeros hidrofobamente modificados incluyen, pero no están limitados a, oxígeno, nitrógeno, azufre o fósforo.

Los polímeros hidrofobamente modificados se pueden sintetizar utilizando cualquier método adecuado. En un ejemplo, los polímeros hidrofobamente modificados pueden ser un producto de reacción de un polímero hidrofílico y un compuesto hidrofobo. En otro ejemplo, los polímeros hidrofobamente modificados se pueden preparar de una reacción de polimerización que comprende un monómero hidrofílico y un monómero hidrofílico hidrofobamente modificado. Aquellos expertos en la técnica, con el beneficio de esta descripción, serán capaces de determinar otros métodos adecuados para la síntesis de polímeros hidrofobamente modificados adecuados.

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En ciertas modalidades, los polímeros hidrófobamente modificados adecuados se pueden sintetizar mediante la modificación hidrofóbica de un polímero hidrofílico. Los polímeros hidrofílicos adecuados para la formación de los polímeros hidrófobamente modificados utilizados en la presente invención deben

5 ser capaces de reaccionar con los compuestos hidrófobos. Los polímeros hidrofílicos adecuados incluyen, homo, co, o terpolímeros tal como, pero no limitados a, poliacrilamidas, polivinilaminas, poli(vinilaminas/vinil alcoholes), polímeros de alquil acrilato en general, y derivados de éste. Ejemplos adicionales de los polímeros de alquil acrilato incluyen, pero no están limitados a,

10 polidimetilaminoetil metacrilato, polidimetilaminopropil metacrilamida, poli(acrilamida/dimetilaminoetil metacrilato), poli(ácido metacrílico/dimetilaminoetil metacrilato), poli(ácido 2-acrilamido-2-metil propano sulfónico/dimetilamino etil metacrilato), poli(acrilamida/dimetilaminopropil metacrilamida), poli (ácido acrílico/dimetilaminopropil metacrilamida), y poli(ácido

15 metacrílico/dimetilaminopropil metacrilamida). En ciertas modalidades, los polímeros hidrofílicos comprenden una estructura de polímero y grupos amino reactivos en la estructura del polímero o como grupos colgantes, los grupos amino reactivos capaces de reaccionar con los compuestos hidrofóbicos. En algunas modalidades, los polímeros hidrofílicos comprenden grupos colgantes dimetil

20 amino y un monómero que comprende dimetilaminoetil metacrilato o dimetilaminopropil metacrilamida. En ciertas modalidades de la presente invención, los polímeros hdirofílicos comprenden una estructura de polímero que comprende heteroátomos polares, en donde los heteroátomos polares presentes dentro de la estructura del polímero de los polímeros hidrofílicos incluyen, pero no

25 están limitados a, oxígeno, nitrógeno, azufre, o fósforo. Los polímeros hidrofílicos adecuados que comprenden los heteroátomos polares dentro de la estructura del polímero incluye homo, co, o terpolímeros, tal como, pero no limitados a,

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celulosas, chitosans, poliamidas, polieteteraminas, polietilenoiminas, polihidroxieteraminas, polilisinas, polisulfonas, gomas, almidones, y derivados de éstos. En una modalidad, el almidón es un almidón catiónico. Un almidón catiónico adecuado se puede formar al hacer reaccionar un almidón, tal como maíz, maíz, 5 maíz ceroso, papa, y tapioca, y similares con el producto de reacción de epíclorohidrina y trialquilamina.

Los compuestos hidrófobos que son capaces de reaccionar con los polímeros hidrofílicos de la presente invención incluyen, pero no están limitados a, 10 alquil haluros, sulfonatos, sulfatos, ácidos orgánicos, y derivados de ácido orgánico. Ejemplos de ácidos orgánicos adecuados y derivados de éstos incluyen, pero no están limitados a, ácido octenil succínico; ácido dodecenil succínico; y anhídridos, éteres, imidas, y amidas de ácido octenil succínico o ácido dodecenil succínico. En ciertas modalidades, los compuestos hidrófobos pueden tener una 15 longitud de cadena de alquilo de desde aproximadamente 4 a aproximadamente 22 carbonos. En otra modalidad, los compuestos hidrófobos pueden tener una longitud de cadena de alquilo de desde aproximadamente 7 a aproximadamente 22 carbonos. En otra modalidad, los compuestos hidrófobos pueden tener una longitud de cadena de alquilo de desde aproximadamente 12 a aproximadamente 20 18 carbonos. Por ejemplo, donde el compuesto hidrófobo es un haluro de alquilo, la reacción entre el compuesto hidrófobo y el polímero hidrofílico puede dar como resultado la cuaternización de por lo menos algunos de los grupos amino de polímero hidrofílico con un haluro de alquilo, en donde la longitud de la cadena de alquilo va de aproximadamente 4 a aproximadamente 22 carbonos.

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Como se mencionó previamente, en ciertas modalidades, los polímeros hidrófobamente modificados adecuados también se pueden preparar de una

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reacción de polimerización que comprende un monómero hidrofílico y un monómero hidrofílico hidrófobamente modificado. Ejemplos de métodos adecuados de su preparación se describen en la Patente U.S. Número 6,476,169, cuya descripción relevante se incorpora aquí como referencia. Los polímeros

5 hidrófobamente modificados sintetizados de las reacciones de polimerización pueden tener pesos moleculares estimados en el rango de desde aproximadamente 100,000 a aproximadamente 10,000,000 y las proporciones en mol de monómero(s) hidrofílico a monómero(s) hidrofílico hidrófobamente modificado en el rango de desde aproximadamente 99.98:0.02 a

10 aproximadamente 90:10.

Una variedad de monómeros hidrofílicos se puede utilizar para formar los polímeros hidrófobamente modificados útiles en la presente invención. Ejemplos de monómeros hidrofílicos adecuados incluyen, pero no están limitados a

15 acrilamida, ácido 2-acrilamido-2-metil propano sulfónico, N,N-dimetilacrilamida, vinil pirrolidona, dimetilaminoetil metacrilato, ácido acrílico, dimetilaminopropilmetacrilamida, vinil amina, vinil acetato, cloruro de trimetilamonioetil metacrilato, metacrilamida, hidroxietil acrilato, ácido vinil sulfónico, ácido vinil fosfónico, ácido metacrílico, vinil caprolactama, N-

20 vinilformamida, N,N-dialilacetamida, haluro de dimetildialil amonio, ácido itacónico, ácido estireno sulfónico, haluro de metacrilamidoetiltrimetil amonio, derivados de sal cuaternaria de acrilamida, y derivados de sal cuaternaria de ácido acrílico.

Una variedad de monómeros hidrofílicos hidrófobamente modificados

25 también se pueden utilizar para formar los polímeros hidrófobamente modificados útiles en la presente invención. Ejemplos de monómeros hidrofílicos hidrófobamente modificados adecuados incluyen, pero no están limitados a, alquil

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acrilatos, alquil metacrilatos, alquil acrilamidas, haluros de alquil metacrilamidas alquil dimetilamonioetil metacrilato, y haluros de alquil dimetilamonioetil metacrilamida, en donde los grupos alquilo tienen desde aproximadamente 4 a aproximadamente 22 átomos de carbono. En otra modalidad, los grupos alquilo tienen desde aproximadamente 7 a aproximadamente 22 carbonos. En otra modalidad, los grupos alquilo tienen desde aproximadamente 12 a aproximadamente 18 carbonos. En ciertas modalidades, el monómero hidrofílico hidrófobamente modificado comprende bromuro de octadecildimetilamonioetil metacrilato, bromuro de hexadecildimetilamonioetil metacrilato, bromuro de hexadecildimetilamonioetil metacrilamida, 2-etilhexil metacrilato, o hexadecil metacrilamida.

Los polímeros hidrófobamente modificados adecuados que se pueden formar de las reacciones anteriormente descritas incluyen, pero no están limitados a, copolímero de acrilamida/bromuro de octadecildimetilamonioetil metacrilato, terpolímero de dimetilaminoetil metacrilato/vinil pirrolidona/bromuro de hexadecildimetilamonioetil metacrilato, y terpolímero de acrilamida/ ácido 2-acrilamido-2-metil propano sulfónico/2-etilhexil metacrilato. Otro polímero hidrófobamente modificado adecuado formado de la reacción anteriormente descrito comprende un copolímero de amino metacrilato/alquil amino metacrilato. Un copolímero de dimetilaminoetil metacrilato/alquildimetilamonioetil metacrilato adecuado es un copolímero dimetilaminoetil metacrilato/hexadecil-dimetilaminoetil metacrilato. Como se discutió previamente, estos copolímeros se pueden formar mediante reacciones con una variedad de haluros de alquilo. Por ejemplo, en algunas modalidades, el polímero hidrófobamente modificado puede comprender un copolímero de dimetilaminoetil metacrilato/bromuro de hexadecil-dimetilamonioetil metacrilato.

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En otra modalidad de la presente invención, los aditivos de control de pérdida de fluido de la presente invención pueden comprender un polímero hidrofílicamente modificado soluble en agua. Los polímeros hidrofílicamente modificados de la presente invención tienen típicamente pesos moleculares en el rango de desde aproximadamente 100,000 a aproximadamente 10,000,000. En ciertas modalidades, los polímeros hidrofílicamente modificados comprenden una estructura de polímero que comprenden heteroátomos polares. En general, los heteroátomos polares presentes dentro de la estructura del polímero de los polímeros hidrofílicamente modificados incluyen, pero no están limitados a, oxígeno, nitrógeno, azufre, o fósforo.

Los polímeros hidrofílicamente modificados se pueden sintetizar utilizando cualquier método adecuado. En un ejemplo, los polímeros hidrofílicamente modificados pueden ser un producto de reacción de un polímero hidrofílico y un compuesto hidrofílico. Aquellos medianamente expertos en la técnica, con el beneficio de esta descripción, serán capaces de determinar otros métodos adecuados para la preparación de polímeros hidrofílicamente modificados adecuados.

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En ciertas modalidades, los polímeros hidrofílicamente modificados adecuados se pueden formar mediante la modificación hidrofílica adicional, por ejemplo, al introducir ramificación o al incrementar el grado de ramificación, de un polímero hidrofílico. Los polímeros hidrofílicos adecuados para formar los polímeros hidrofílicamente modificados utilizados en la presente invención deben ser capaces de reaccionar con los compuestos hidrofílicos. En ciertas modalidades, los polímeros hidrofílicos adecuados incluyen, homo, co, o

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terpolímeros, tales como, pero no limitados a, poliacrilamidas, polivinilaminas, poli(vinilaminas/vinil alcoholes), y polímeros de alquil acrilato en general. Ejemplos adicionales de polímeros de alquil acrilato incluyen, pero no están limitados a, polidimetilaminoetil metacrilato, polidimetilaminopropil metacrilamida, 5 poli(acrilamida/dimetilaminoetil metacrilato), poli(ácido metacrílico/dimetilaminoetil metacrilato), poli(ácido 2-acrilamido-2-metil propano sulfónico/dimetilamino etil metacrilato), poli(acrilamida/dimetilaminopropil metacrilamida), poli (ácido acrílico/dimetilaminopropil metacrilamida), y poli(ácido metacrílico/dimetilaminopropil metacrilamida). En ciertas modalidades, los 10 polímeros hidrofílicos comprenden una estructura de polímero y grupos amino reactivos en la estructura de polímero o como grupos colgantes, los grupos amino reactivos capaces de reaccionar con los compuestos hidrofílicos. En algunas modalidades, los polímeros hidrofílicos comprenden grupos colgantes dialquil amino. En algunas modalidades, los polímeros hidrofílicos comprenden un grupo 15 colgante dimetil amino y por lo menos un monómero que comprende dimetilaminoetil metacrilato o dimetilaminopropil metacrilamida. En otras modalidades, los polímeros hdrofílicos comprenden una estructura de polímero que comprende heteroátomos polares, en donde los heteroátomos polares presentes dentro de la estructura del polímero de los polímeros hidrofílicos 20 incluyen, pero no están limitados a, oxígeno, nitrógeno, azufre, o fósforo. Los polímeros hidrofílicos adecuados que comprenden los heteroátomos polares dentro de la estructura del polímero incluye homo, co, o terpolímeros, tales como, pero no limitados a, celulosas, chitosans, poliamidas, polieteteraminas, polietilenoiminas, polihidroxieteraminas, polilisinas, polisulfonas, gomas, 25 almidones, y derivados de éstos. En una modalidad, el almidón es un almidón catiónico. Un almidón catiónico adecuado se puede formar al hacer reaccionar un

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almidón, tal como maíz, maíz, maíz ceroso, papa, tapioca, y similares con el producto de reacción de epiclorohidrina y trialquilamina.

Los compuestos hidrofílicos adecuados para la reacción con los polímeros

5 hidrofílicos incluyen poliéteres que comprenden halógenos, sulfonatos, sulfatos, ácidos orgánicos, y derivados de ácido orgánico. Ejemplos de poliéteres adecuados incluyen, pero no están limitados a, óxidos de polietileno, óxidos de polipropileno, y óxidos de polibutileno, y copolímeros, terpolímeros, y mezclas de éstos. En algunas modalidades, el poliéter comprende un metil éter de óxido de

10 polietileno terminado en epiclorohidrina.

Los polímeros hidrofílicamente modificados formados de la reacción de un polímero hidrofílico con un compuesto hidrofílico puede tener pesos moleculares estimados en el rango de desde aproximadamente 100,000 a aproximadamente

15 10,000,000 y puede tener proporciones en peso de los polímeros hidrofílicos a los poliéteres en el rango de desde aproximadamente 1:1 a aproximadamente 10:1. Los polímeros hidrofílicamente modificados adecuados que tienen pesos moleculares y proporciones en peso en los rangos establecidos anteriormente incluyen, pero no están limitados a, el producto de reacción del polidimetilaminoetil

20 metacrilato y el polietilenóxido metil éter terminado en epiclorohidrina; el producto de reacción de la polidimetilaminopropil metacrilamida y el polietilenóxido metil éter terminado en epiclorohidrina; y el producto de reacción de poli(acrilamida/dimetilaminopropil metacrilamida) y el polietilenóxido metil éter terminado en epiclorohidrina. En algunas modalidades, el polímero

25 hidrofílicamente modificado comprende el producto de reacción de un polidimetilaminoetil metacrilato y polietilenóxido metil éter terminado en epiclorohidrina que tiene una proporción en peso de polidimetilaminoetil

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metacrilato a polietilenóxido metil éter terminado en epiclorohidrina de aproximadamente 3:1.

Las concentraciones suficientes de los aditivos de control de pérdida de fluido de la presente invención deben estar presentes en fluidos de tratamiento de la presente invención para suministrar el nivel deseado de control de pérdida de fluido. En algunas modalidades, los aditivos de control de pérdida de fluido deben estar presentes en los fluidos de tratamiento de la presente invención en una cantidad en el rango de desde aproximadamente 0.02% a aproximadamente 10% en peso del fluido de tratamiento. En otra modalidad, el aditivo de control de pérdida de fluido debe estar presente en los fluidos de tratamiento de la presente invención en una cantidad en el rango de desde aproximadamente 0.05% a aproximadamente 1.0% en peso del fluido de tratamiento. En ciertas modalidades de la presente invención, el aditivo de control de pérdida de fluido se puede suministrar en una solución acuosa concentrada antes de su combinación con los otros componentes necesarios para formar los fluidos de tratamiento de la presente invención.

Los aditivos adicionales se pueden agregar a los fluidos de tratamiento de la presente invención según se considere apropiado para una aplicación particular por un experto en la técnica con el beneficio de esta descripción. Ejemplos de tales aditivos incluyen, pero no están limitados a, agentes densificantes, tensoactivos, inhibidores de incrustaciones, agentes antiespumantes, bactericidas, sales, agentes espumantes, ácidos, aditivos de control de pérdida de fluido convencionales, agentes viscosificantes, agentes reticulantes, rompedores de gel, inhibidores de hinchamiento de shale, combinaciones de éstos, y similares.

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Los fluidos de tratamiento de la presente invención se pueden utilizar en tratamientos subterráneos donde sea deseable suministrar control de pérdida de fluido. En general, los aditivos de control de pérdida de fluido se pueden utilizar en cualquier etapa de un tratamiento subterráneo. En ciertas modalidades, el fluido de tratamiento puede ser un fluido de perforación, un fluido de fracturamiento, un fluido de re-acondicionamiento, un fluido de limpieza de perforación, un fluido de relleno de cascajo, o cualquier otro fluido acuoso adecuado utilizado en los tratamientos subterráneos. En otra modalidad, los fluidos de tratamiento pueden ser una píldora de control de pérdida de fluido que se introduzca en la perforación en cualquier etapa del tratamiento subterráneo. Por ejemplo, el fluido de tratamiento puede ser un preflujo que se introduzca en la perforación antes del tratamiento subterráneo.

En general, los métodos de la presente invención comprenden introducir un fluido de tratamiento de la presente invención que comprenda un fluido acuoso y un aditivo de control de pérdida de fluido que comprenda un polímero soluble en agua con una modificación hidrófoba o hidrofílica en una perforación que penetre una formación subterránea con el fin de reducir la pérdida de fluido en por lo menos una porción de la formación subterránea proveniente del fluido de tratamiento u otro fluido acuoso introducido en la perforación posterior al fluido de tratamiento. En general, por lo menos una porción del fluido de tratamiento debe penetrar en la porosidad de por lo menos una porción de la formación subterránea a por lo menos alguna profundidad de la superficie tratada durante la chorreadura normal proveniente del fluido de tratamiento. Se cree que el polímero soluble en agua presente en la porción del fluido de tratamiento que chorrea desde la formación debe unirse a las superficies dentro de la porosidad de la porción de la formación subterránea. La presencia de los polímeros solubles en agua allí debe