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(54) Title: TREATMENT FLUIDS CONTAINING A RELATIVE PERMEABILITY MODIFIER AND A COMPANION POLYMER INTERACTING SYNERGISTICALLY THEREWITH AND METHODS FOR USE THEREOF

(57) Abstract: Methods and compositions are described for treating water- and hydrocarbon-producing subterranean formations with a relative permeability modifier at concentrations below those conventionally used in the art, while not substantially impacting the treatment fluid's performance. Treatment fluids described herein comprise a base fluid, a relative permeability modifier comprising a hydrophobically modified hydrophilic polymer, and a companion polymer interacting synergistically with the relative permeability modifier such that the treatment fluid is operable to reduce the water permeability or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation by more than the relative permeability modifier or the companion polymer acting alone at like concentration. The water permeability reduction and/or the aqueous fluid injection pressure increase can be more than additive. Methods described herein comprise placing such treatment fluids in at least a portion of a subterranean formation.

TREATMENT FLUIDS CONTAINING A RELATIVE PERMEABILITY MODIFIER AND A COMPANION POLYMER INTERACTING SYNERGISTICALLY THEREWITH AND METHODS FOR USE THEREOF

BACKGROUND

[0001] The present invention relates to methods and compositions for treating at least a portion of a water- and hydrocarbon-producing subterranean formation with a relative permeability modifier, and, more specifically, to improved treatment fluids and methods for use thereof in which concentrations of the relative permeability modifier are appreciably below those conventionally used in the art, while not substantially impacting the treatment fluid's effectiveness to reduce the water permeability or to increase an aqueous fluid injection pressure of the treated portion of the subterranean formation.

[0002] The unwanted production of water from hydrocarbon-producing wells constitutes a considerable technical problem and expense in oilfield operations. When a subterranean formation contains water in significant amounts, water's higher mobility often allows it to flow to a well bore penetrating the formation by way of natural and manmade fractures and high permeability zones. If the ratio of recovered water to recovered hydrocarbons becomes sufficiently large, the cost of separating the water from the hydrocarbons and disposing of it can become a barrier to continued production. This can lead to abandonment of a well penetrating a subterranean formation, even when significant amounts of hydrocarbons remain therein.

[0003] In order to reduce the undesired production of water from hydrocarbon-producing subterranean formations, aqueous-soluble polymer systems containing crosslinking agents have been utilized in the art to enter water-containing zones of the formation and block the flow of water therefrom. Selective placement of these crosslinked polymers in a subterranean formation and stability therein represent significant technical challenges that have somewhat limited their use. A more recent strategy to reduce water production from a subterranean formation has been to utilize agents known as relative permeability modifiers. Such relative permeability modifiers are capable of significantly reducing the flow of water from a subterranean formation while having a minimal effect on the flow of hydrocarbons. The use of relative permeability modifiers does not necessitate the use of zonal isolation techniques that are often employed with crosslinked polymers.

[0004] Relative permeability modifiers can also be used to pre-treat a subterranean formation and divert the flow of a subsequently added aqueous treatment fluid therein.

Diversion of the treatment fluid flow in such cases is primarily accomplished by increasing the injection pressure of the treatment fluid. Unless diverted, the injected aqueous treatment fluid often takes the path of least resistance through the subterranean formation by flowing through high permeability pathways from the injector and can bypass the desired treatment zones. In applications such as enhanced oil recovery (EOR) methods, aqueous fluid chemical flooding techniques are frequently used. Unless the chemical flood is diverted to a desired subterranean zone, lower than expected oil production will be realized. Similar effects can be observed when aqueous treatment fluids (*e.g.*, acidizing fluids, scale removal fluids, and the like) are used in treating subterranean formations having significant water permeability.

[0005] From an economic standpoint alone, it would be desirable to decrease the volume of treatment fluid being placed in a subterranean formation and/or to reduce the amount of relative permeability modifier being used in a treatment fluid, while not substantially impacting the treatment fluid's downhole performance for controlling water flow or increasing the aqueous fluid injection pressure of subsequently added treatment fluids.

SUMMARY OF THE INVENTION

[0006] The present invention relates to methods and compositions for treating at least a portion of a water- and hydrocarbon-producing subterranean formation with a relative permeability modifier, and, more specifically, to improved treatment fluids and methods for use thereof in which concentrations of the relative permeability modifier are appreciably below those conventionally used in the art, while not substantially impacting the treatment fluid's effectiveness to reduce the water permeability or to increase an aqueous fluid injection pressure of the treated portion of the subterranean formation.

[0007] According to a first aspect, the present invention provides a method comprising: providing a treatment fluid that comprises: a base fluid; a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and a companion polymer that comprises at least an acrylamide monomer unit; wherein the companion polymer is not hydrophobically modified; and placing the treatment fluid in at least a portion of a subterranean formation.

[0008] Preferably, the treatment fluid is operable to reduce the water permeability of at least a portion of a subterranean formation by at least about 80% or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation above about 100 psi [about 690kPa].

[0009] Preferably, the relative permeability modifier comprises dimethylaminoethyl methacrylate and a monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0010] Preferably, the companion polymer comprises a partially hydrolyzed polyacrylamide having a molecular weight of greater than about 10,000,000, a partially hydrolyzed polyacrylamide having a molecular weight of less than about 500,000, an acrylamide/diallyldimethylammonium chloride copolymer, a polyethyleneimine, or a diutan.

[0011] According to another aspect, the present invention provides a method comprising: providing a treatment fluid that comprises: a base fluid; a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and a companion polymer interacting synergistically with the relative permeability modifier such that the treatment fluid is operable to reduce the water permeability or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation by more than through using the relative permeability modifier or the companion polymer acting alone at like concentration; and placing the treatment fluid in at least a portion of a subterranean formation.

[0012] Preferably, the treatment fluid is operable to reduce the water permeability of the portion of the subterranean formation by at least about 80%; and a concentration of the relative permeability modifier in the treatment fluid is only operable to reduce the water permeability of the portion of the subterranean formation by about 5% to about 80% without the companion polymer.

[0013] Preferably, the treatment fluid is operable to reduce the water permeability of the portion of the subterranean formation by more than an additive water permeability reduction or to increase the aqueous fluid injection pressure of the portion of the subterranean formation by more than an additive aqueous fluid injection pressure increase obtained from the relative permeability modifier and the companion polymer, each acting independently.

[0014] Preferably, the hydrophobically modified hydrophilic polymer comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0015] Preferably, the companion polymer is not hydrophobically modified.

[0016] Preferably, the companion polymer comprises at least one of a cationic, an anionic or a non-ionic polymer.

[0017] Preferably, the companion polymer comprises at least one polymer selected from the group consisting of a polyacrylate, a polyacrylamide, an acrylate/acrylamide copolymer, an acrylamide/diallyldimethylammonium chloride copolymer, a diutan, and polyethylenimine.

[0018] Preferably, the companion polymer comprises at least one of an acrylamide monomer unit or an acrylate ester monomer unit.

[0019] Preferably, at least a portion of the side chains of the companion polymer are hydrolyzed.

[0020] Preferably the relative permeability modifier comprises dimethylaminoethyl methacrylate and a monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0021] Preferably, the companion polymer comprises a partially hydrolyzed polyacrylamide having a molecular weight of greater than about 10,000,000, a partially hydrolyzed polyacrylamide having a molecular weight of less than about 500,000, an acrylamide/diallyldimethylammonium chloride copolymer, a polyethyleneimine, or a diutan.

[0022] According to another aspect, the present invention provides a method comprising: providing a treatment fluid that comprises: a base fluid; a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and a companion polymer that comprises at least an acrylamide monomer unit; wherein the companion polymer is not hydrophobically modified; placing the treatment fluid in at least a portion of a subterranean formation; and allowing the treatment fluid to reduce a water permeability or to increase an aqueous fluid injection pressure of the portion of the subterranean formation.

[0023] Preferably, the hydrophobically modified hydrophilic polymer comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0024] Preferably, the treatment fluid is operable to reduce the water permeability of the portion of the subterranean formation by at least about 80%; and

a concentration of the relative permeability modifier in the treatment fluid is only operable to reduce the water permeability of the portion of the subterranean formation by about 5% to about 80% without the companion polymer.

[0025] Preferably, at least a portion of the side chains of the companion polymer are hydrolyzed.

[0026] Preferably the relative permeability modifier comprises dimethylaminoethyl methacrylate and a monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0027] Preferably, the companion polymer comprises a partially hydrolyzed polyacrylamide having a molecular weight of greater than about 10,000,000, a partially hydrolyzed polyacrylamide having a molecular weight of less than about 500,000, or an acrylamide/diallyldimethylammonium chloride copolymer.

[0028] According to another aspect, the present invention provides a method comprising: providing a treatment fluid that comprises: a base fluid; a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer comprising at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide; wherein a concentration of the relative permeability modifier in the treatment fluid is below its normal effective working concentration; and a companion polymer; and wherein the treatment fluid is operable to reduce the water permeability of at least a portion of a subterranean formation by at least about 80% or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation above about 100 psi [about 690 kPa]; and placing the treatment fluid in at least a portion of a subterranean formation.

[0029] Preferably, the companion polymer is not hydrophobically modified.

[0030] Preferably, the companion polymer comprises at least one polymer selected from the group consisting of a polyacrylate, a polyacrylamide, an acrylate/acrylamide copolymer, and an acrylamide/diallyldimethylammonium chloride copolymer.

[0031] Preferably, at least a portion of the side chains of the companion polymer are hydrolyzed.

[0032] Preferably, the companion polymer comprises at least one polymer selected from the group consisting of a diutan and polyethylenimine.

[0033] Preferably the relative permeability modifier comprises dimethylaminoethyl methacrylate and a monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0034] Preferably, the companion polymer comprises a partially hydrolyzed polyacrylamide having a molecular weight of greater than about 10,000,000, a partially hydrolyzed polyacrylamide having a molecular weight of less than about 500,000, an acrylamide/diallyldimethylammonium chloride copolymer, a polyethyleneimine, or a diutan.

[0035] According to another aspect, the present invention provides a treatment fluid comprising: a base fluid; a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and a companion polymer interacting synergistically with the relative permeability modifier such that the treatment fluid is operable to reduce the water permeability or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation by more than through using the relative permeability modifier or the companion polymer acting alone.

[0036] Preferably, the companion polymer comprises at least one polymer selected from the group consisting of a polyacrylamide, a polyacrylate, an acrylamide/acrylate copolymer, an acrylamide/diallyldimethyl ammonium chloride copolymer, a diutan, and a polyethyleneimine.

[0037] Preferably the relative permeability modifier comprises dimethylaminoethyl methacrylate and a monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

[0038] Preferably, the companion polymer comprises a partially hydrolyzed polyacrylamide having a molecular weight of greater than about 10,000,000, a partially hydrolyzed polyacrylamide having a molecular weight of less than about 500,000, an acrylamide/diallyldimethylammonium chloride copolymer, a polyethyleneimine, or a diutan.

[0039] The features and advantages of the present invention will be readily apparent to one of ordinary skill in the art upon a reading of the description of the preferred embodiments that follows.

DETAILED DESCRIPTION

[0040] The present invention relates to methods and compositions for treating at least a portion of a water- and hydrocarbon-producing subterranean formation with a relative permeability modifier, and, more specifically, to improved treatment fluids and methods for use thereof in which concentrations of the relative permeability modifier are appreciably below those conventionally used in the art, while not substantially impacting the treatment fluid's effectiveness to reduce the water permeability or to increase an aqueous fluid injection pressure of the treated portion of the subterranean formation.

[0041] There are many advantages of the present invention, only a few of which are discussed or alluded to herein. The present invention provides treatment fluid compositions and methods for use thereof in which relative permeability modifiers are used in considerably lower concentrations than are conventional in the art, while still providing comparable downhole performance. This can result in beneficial reductions in cost of goods and, perhaps more importantly, lessened environmental impacts when treating a subterranean formation. Specifically, the combination of a relative permeability modifier and a companion polymer may produce a water permeability reduction and/or increase an aqueous fluid injection pressure (*i.e.*, increased resistance to aqueous fluid flow) in at least a portion of a subterranean formation that is comparable to that seen when higher concentrations of relative permeability modifier are used without the companion polymer being present. The present invention can allow lower total polymer concentrations or amounts (*e.g.*, the combined concentration or amounts of the relative permeability modifier and the companion polymer) to be used in the treatment fluid in order to obtain a downhole water permeability reduction and/or increased aqueous fluid injection pressure that is comparable to that seen with higher concentrations of the relative permeability modifier alone.

[0042] It is believed that the combination of the relative permeability modifier and the companion polymer in the present treatment fluids can surprisingly produce a water permeability reduction and/or increased aqueous fluid injection pressure in at least a portion of a subterranean formation that is greater than the additive effect of the relative permeability modifier and the companion polymer acting independently. That is, in the present treatment fluids, a greater reduction in water permeability and/or increased aqueous fluid injection pressure can be realized than through the independent use of separate treatment fluids containing the relative permeability modifier or the companion polymer alone at like concentrations. Without being bound by theory or mechanism, it is believed that this unexpected result arises from a synergistic interaction between the relative permeability modifier and the companion polymer resulting from a polymer complex that forms through a hydrogen bonding interaction or ionic association between suitable functional groups of the relative permeability modifier and the companion polymer. Examples of polymer functional groups that are suitable for hydrogen bonding can include a neutral or protonated amine on a first polymer chain and a hydroxyl group or a carboxylate anion on a second polymer chain. Examples of polymer functional groups that are suitable for forming an ionic association include quaternary ammonium ions on a first polymer chain and a carboxylate anion on a second polymer chain.

[0043] Concerns have recently been raised regarding the environmental impact of treatment fluids used during various subterranean operations. Since the treatment fluids of the present invention contain lower concentrations or amounts of relative permeability modifier than do conventional treatment fluids, the present treatment fluids may be particularly advantageous from an environmental standpoint.

[0044] Still further, because the present treatment fluids contain much lower concentrations or amounts of relative permeability modifier than are conventionally used in the art, they can be used in subterranean formations having conditions (*e.g.*, high or low pH and/or temperature) under which higher concentrations or amounts of the relative permeability modifier can become unstable. For example, under certain conditions, some relative permeability modifiers can precipitate from a treatment fluid. The stability of the present treatment fluids can be further enhanced through various additives, as described in more detail below.

[0045] The present treatment fluids and methods can advantageously be used in any of the production stage, the stimulation stage, EOR operations, or the remediation stage of a subterranean operation to address downhole water or injected aqueous fluids. As defined herein, a "treatment fluid" is a fluid that is placed in a subterranean formation in order to perform a desired function. Treatment fluids can be used in a variety of subterranean operations, including, but not limited to, production treatments, stimulation treatments, remedial treatments, fluid diversion operations, fracturing operations, secondary or tertiary EOR operations, and the like. As used herein, the terms "treatment" and "treating" refer to any subterranean operation that uses a fluid in conjunction with performing a desired function and/or achieving for a desired purpose. The terms "treatment" and "treating," as used herein, do not imply any particular action by the fluid or any particular component thereof unless otherwise specified. Treatment fluids can include, without limitation, fracturing fluids, acidizing fluids, conformance treatments, damage control fluids, remediation fluids, scale removal and inhibition fluids, chemical floods, and the like.

[0046] Treatment fluids of the present invention generally comprise an aqueous phase base fluid. Aqueous phase base fluids can include, for example, fresh water, acidified water, salt water, seawater, brine, or an aqueous salt solution. Preferably, the treatment fluids can also contain small amounts of hydrocarbons such that the aqueous base fluid remains as the continuous phase. Specifically, certain companion polymers described herein are obtained in a hydrocarbon base fluid. Inclusion of small amounts of hydrocarbons from the companion polymer source does not significantly impact the performance of the present treatment fluids.

[0047] The treatment fluids of the present invention may include an aqueous phase base fluid as the continuous phase. Preferably, the aqueous phase base fluid can be an aqueous salt solution. Such aqueous salt solutions can have a salt concentration ranging between about 0.1% and about 10% by weight. The salt concentration may range between about 1% and about 10% by weight, or it may range between about 2% and about 5% by weight. The treatment fluids of the present invention may comprise a base fluid, a relative permeability modifier and a companion polymer that interacts synergistically with the relative permeability modifier. In general, the relative permeability modifier comprises a hydrophobically modified hydrophilic polymer. The synergistic interaction between the relative permeability modifier and the companion polymer is such that the treatment fluid is operable to reduce the water permeability of at least a portion of a subterranean formation by more than through using the relative permeability modifier or the companion polymer acting alone at like concentration. Alternately, the synergistic interaction between the relative permeability modifier and the companion polymer is such that the treatment fluid is operable to increase the aqueous fluid injection pressure of an aqueous treatment fluid (*e.g.*, an acidizing fluid, an EOR fluid, and the like) by more than through using the relative permeability modifier or the companion polymer acting alone at like concentration.

[0048] Preferably, the treatment fluid is operable to reduce the water permeability of the portion of the subterranean formation by at least about 80%. The reduction in water permeability may be at least about 85%, or it may be at least about 90%, or it may be at least about 95%, or it may be at least about 98%, or it may be at least about 99%. The water permeability reduction can be due to a synergistic interaction between the relative permeability modifier and the companion polymer. A concentration of the relative permeability modifier in the treatment fluid may be only operable to reduce the water permeability of the subterranean formation by about 5% to about 80% without the companion polymer.

[0049] Measurement of the water permeability reduction of a subterranean formation can be determined by measuring the permeability reduction of a core sample obtained from the subterranean formation. Illustrative methods for determining the water permeability reduction of a subterranean formation core sample are described in United States Patent 6,476,169, which is incorporated herein by reference in its entirety. An untreated core sample has no water permeability reduction. Increases in aqueous fluid injection pressure can be determined by like methods through measuring the pressure increase in the core sample following administration of the treatment fluid.

[0050] Preferably, the treatment fluid is operable to increase the injection pressure of an aqueous treatment fluid into the portion of the subterranean formation by about 50% to about 500% compared to that achievable using the relative permeability modifier or the companion polymer acting alone. A concentration or amount of the relative permeability modifier and the companion polymer in the treatment fluid may be only operable to increase the aqueous fluid injection pressure by about 1% to about 10% when the relative permeability modifier or the companion polymer is used alone. The amount of relative permeability modifier in the treatment fluid needed to achieve a given aqueous fluid injection pressure increase may be only about 20% to about 50% of that needed when the companion polymer is absent.

[0051] Determining that a synergistic interaction exists between a relative permeability modifier and a companion polymer to produce a water permeability reduction or increase in aqueous fluid injection pressure that is more than additive can be ascertained as described for the following non-limiting prophetic examples. The water permeability reduction or aqueous fluid injection pressure increase of the subterranean formation may be able to be assessed by measuring the water permeability reduction or aqueous fluid injection pressure increase of a core sample or column packed with a suitable particulate material (*e.g.*, sand or calcium carbonate) as referenced above. It is to be presumed that the reduction in water permeability or increase in aqueous fluid injection pressure of the core sample is representative of the subterranean formation as a whole.

[0052] Prophetic Example 1: Consider a treatment fluid containing a relative permeability modifier and a companion polymer that produces a water permeability reduction of 95%. Further consider treatment fluids of like composition and concentration containing only the relative permeability modifier or the companion polymer, but not both, in which the water permeability reduction produced is 10% and 50%, respectively. In such an example, one of ordinary skill in the art should expect a water permeability reduction of only about

60% in the combined treatment fluid, if the effects of the relative permeability modifier and the companion polymer were simply additive in nature. If the water permeability reduction is considerably higher, as in the present example, the relative permeability modifier and the companion polymer can be considered to be interacting synergistically to produce a non-additive water permeability reduction.

[0053] Prophetic Example 2: Consider a treatment fluid containing a relative permeability modifier and a companion polymer that produces a water permeability reduction of 95%. Further consider treatment fluids of like composition and concentration containing only the relative permeability modifier or the companion polymer, but not both, in which the water permeability reduction produced is 70% and 50%, respectively. In this example, the additive water permeability reduction of the combined treatment fluid sums to more than 100%, and a synergistic interaction between the relative permeability modifier and the companion polymer may not be directly detected due to the tested concentrations being too high, although the concept of a synergistic interaction can still apply. In cases where the additive water permeability reduction sums to more than 100% or sums to very nearly 100%, the tested concentrations can be lowered and the treatment fluids retested to determine if the water permeability reduction is indeed more than additive.

[0054] Like prophetic examples for aqueous fluid injection pressure increases that demonstrate a synergistic interaction can be envisioned by one having ordinary skill in the art. It should be noted that aqueous fluid injection pressure increases can be used to directly detect a synergistic interaction, even in cases where the individual water permeability reductions sum to more than 100% (see Prophetic Example 2). Specifically, if the measured aqueous fluid injection pressure of the treatment fluid containing both the relative permeability modifier and the companion polymer is greater than the sum of the aqueous fluid injection pressure of the relative permeability modifier and the companion polymer alone, a synergistic interaction can be indicated.

[0055] It should also be noted that reduction of the water permeability of a portion of a subterranean formation may not necessarily be accompanied by an increase in aqueous fluid injection pressure, even though such effects are frequently observed in concert with one another. For example, a water permeability reduction of greater than about 95% can be achieved without a significant pressure increase. Conversely, an increase in aqueous fluid injection pressure due to treatment of a portion of a subterranean formation does not necessarily indicate that the water permeability has been reduced. For the purposes of this invention, the phenomena may be considered to be unrelated. Preferably, an aqueous fluid injection pressure increase resulting from treatment with a relative permeability modifier allows for diversion of additional relative permeability modifier or other aqueous treatment fluids (*e.g.*, an acidizing fluid or an EOR fluid) into untreated zones.

[0056] The treatment fluids of the present invention may comprise a base fluid, a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer, and a companion polymer that comprises at least an acrylamide monomer unit, where the companion polymer is not hydrophobically modified.

[0057] The treatment fluids of the present invention may comprise a base fluid, a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer that comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide, and a companion polymer. A concentration of the relative permeability modifier in the treatment fluid may be below its normal effective working concentration. The treatment fluid may be operable to reduce the water permeability of at least a portion of a subterranean formation by at least about 80% or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation above about 100 psi [about 690 kPa].

[0058] Preferably, treatment fluids of the present invention are placed in at least a portion of a subterranean formation. Preferably, the treatment fluids are allowed to reduce a water permeability of at least a portion of the subterranean formation or to increase an aqueous fluid injection pressure of at least a portion of the subterranean formation.

[0059] Preferably, methods of the present invention comprise providing a treatment fluid that comprises a base fluid, a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer, and a companion polymer that interacts synergistically with the relative permeability modifier such that the treatment fluid is operable to reduce the water permeability or increase an aqueous fluid injection pressure of at least a portion of a subterranean formation by more than through using the relative permeability modifier or the companion polymer acting alone; and placing the treatment fluid in at least a portion of a subterranean formation.

[0060] Preferably, methods of the present invention comprise providing a treatment fluid that comprises a base fluid, a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer, and a companion polymer that comprises at least an acrylamide monomer unit; and placing the treatment fluid in at least a portion of a subterranean formation. In such treatment fluids, the companion polymer is not hydrophobically modified. Preferably, the methods further include allowing the treatment fluid to reduce a water permeability or to increase an aqueous fluid injection pressure of the portion of the subterranean formation.

[0061] As used herein, the term "not hydrophobically modified" refers to a base polymer that does not contain a hydrophobic modification thereon. As used herein, a hydrophobic modification of a base polymer will be considered to be any hydrophobic group having more than about 4 carbon atoms.

[0062] Preferably, methods of the present invention comprise providing a treatment fluid that comprises a base fluid, a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer that comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide, and a companion polymer; and placing the treatment fluid in at least a portion of a subterranean formation. In such treatment fluids, a concentration of the relative permeability modifier in the treatment fluid can be below its normal effective working concentration. Further, preferably, the treatment fluid can be operable to reduce the water permeability of at least a portion of the subterranean formation by at least about 80% or to increase an aqueous fluid injection pressure of at least a portion of the subterranean formation above about 100 psi [about 690 kPa]. Preferably, a concentration and/or amount of the relative permeability modifier in the treatment fluid is only operable to increase the aqueous fluid injection pressure by about 1% to about 10% of the value achievable when used in combination with the companion polymer.

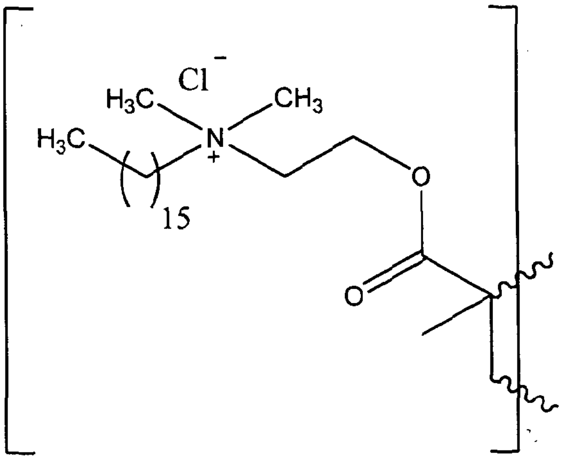
[0063] Relative permeability modifiers used may be hydrophobically modified hydrophilic polymers, which are described in more detail in commonly owned United States Patent 6,476,169, which is incorporated herein by reference in its entirety above. Hydrophobically modified hydrophilic polymers vary widely in structure, but generally comprise a hydrophilic polymer that has been at least partially chemically modified with hydrophobic groups (*e.g.*, long chain alkyl groups having more than about 4 carbon atoms or more than about 6 carbons). An existing hydrophilic polymer may be at least partially functionalized with a plurality of hydrophobic groups to produce a hydrophobically modified hydrophilic polymer. A hydrophilic monomer unit functionalized with a hydrophobic group may be polymerized with itself or copolymerized with a hydrophilic monomer unit not containing hydrophobic functionalization to produce a hydrophobically modified hydrophilic polymer.

[0064] Hydrophobically modified hydrophilic polymers of the present invention may comprise at least one hydrophobically modified hydrophilic monomer and, optionally, at least one hydrophilic monomer. As such, the hydrophobically modified hydrophilic polymers of the present invention may be homopolymers, copolymers, terpolymers or higher order polymer structures. Positioning of the hydrophilic monomer units and the hydrophobically modified hydrophilic monomer units in copolymer and higher order polymer structures can vary without limitation and can be, for example, alternating, random, block or a combination thereof. Examples of suitable hydrophilic monomers include, for example, 2-acrylamido-2-methyl propane sulfonic acid, N,N-dimethylacrylamide, vinyl pyrrolidone, dimethylaminoethyl methacrylate, dimethylaminoethyl methacrylamide, acrylic acid, methacrylic acid, dimethylaminopropyl methacrylate, dimethylaminopropyl methacrylamide, trimethylammoniumethyl methacrylate halide (halide = chloride, bromide, iodide or a halide equivalent such as, for example, a tosylate or methanesulfonate), acrylamide, methacrylamide, and hydroxyethyl acrylate.

[0065] The hydrophobically modified hydrophilic polymers may be prepared by polymerizing at least one hydrophobically modified hydrophilic monomer or a mixture of at least one hydrophobically modified hydrophilic monomer and at least one hydrophilic monomer. Illustrative hydrophobically modified hydrophilic monomers include, for example, alkyl acrylates, alkyl methacrylates, alkyl acrylamides, alkyl methacrylamides, alkyldimethylammoniumethyl methacrylate bromide, alkyldimethylammoniumethyl methacrylate chloride, alkyldimethylammoniumethyl methacrylate iodide, alkyldimethylammoniumpropyl methacrylate bromide, alkyldimethylammoniumpropyl methacrylate chloride, alkyldimethylammoniumpropyl methacrylate iodide, alkyldimethylammoniumethyl methacrylamide bromide, alkyldimethylammoniumethyl methacrylamide chloride, alkyldimethylammoniumethyl methacrylamide iodide, alkyldimethylammoniumpropyl methacrylamide bromide, alkyldimethylammoniumpropyl methacrylamide chloride and alkyldimethylammoniumpropyl methacrylamide iodide. In general, alkyl groups of the hydrophobically modified hydrophilic monomers contain about 4 to about 22 carbon atoms.

[0066] The hydrophobically modified hydrophilic polymer may comprise at least one alkyldimethylammoniumethyl methacrylate halide as the hydrophobically modified hydrophilic monomer. The alkyl group may comprise about 4 to about 22 carbon atoms. The alkyl group may comprise about 6 to about 22 carbon atoms. The halide may be chloride, bromide, iodide, or a halide equivalent (*e.g.*, toluenesulfonate or methanesulfonate), for example. The alkyl group may be a cetyl group containing 16 carbon atoms. That is, a cetyldimethylammoniumethyl methacrylate halide monomer unit may be polymerized to form the hydrophobically modified hydrophilic polymer or a dimethylaminoethyl methacrylate monomer unit in a hydrophilic polymer may be hydrophobically modified with an agent such as, for example, a cetyl halide or a cetyl halide equivalent.

[0067] The relative permeability modifier may be a hydrophobically modified hydrophilic polymer that comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide. Such a relative permeability modifier contains at least the following structural unit in its polymer backbone, where the wavy lines represent bonding to other monomer units.



As noted above, relative permeability modifiers containing this monomer unit can be homopolymers or copolymers or higher order polymer structures containing a hydrophilic monomer. For example, a relative permeability modifier may contain dimethylaminoethyl methacrylate and the above monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide. This relative permeability modifier is sold under the trade name "HPT-1" by Halliburton Energy Services of Duncan, Oklahoma. Specific synthetic procedures and disclosure relating to this relative permeability modifier are described in commonly owned United States Patent 7,114,568, which is incorporated herein by reference in its entirety.

[0068] When not combined with a companion polymer, normal effective working concentrations of most relative permeability modifiers comprising a hydrophobically modified hydrophilic polymer range between about 0.1% and about 3.0% by weight in a treatment fluid. Choice of the normal effective working concentration will be a function of the temperature and porosity of the subterranean formation. Such relative permeability modifiers may have normal effective working concentrations ranging between about 0.2% and about 1.0% by weight in a treatment fluid. In general, such normal effective working concentrations of the relative permeability modifier give a water permeability reduction of greater than about 95% in a subterranean formation. Such normal effective working concentrations of the relative permeability modifier may give aqueous fluid injection pressure increases of about 20 psi [about 140 kPa] to about 500 psi [about 3400 kPa]. At relative permeability modifier concentrations below about 0.1% by weight, a water permeability reduction of less than about 95% or, more particularly, a water permeability reduction of less than about 80% can be obtained. This level of permeability reduction can be ineffective in various subterranean operations. However, relative permeability modifier concentrations below those conventionally used in the art may still produce a water permeability reduction of at least about 80% or even at least about 95% through use of small concentrations of the companion polymer.

[0069] Concentrations of the relative permeability modifier may generally be about 0.15% or lower by weight in the treatment fluid. The concentration of the relative permeability modifier may be about 0.12% or lower by weight in the treatment fluid, or about 0.10% or lower by weight in the treatment fluid, or about 0.08% or lower by weight in the treatment fluid, or about 0.06% or lower by weight in the treatment fluid, or about 0.04% or lower by weight in the treatment fluid, or about 0.02% or lower by weight in the treatment fluid. The concentration of the relative permeability modifier may be about 0.01% or lower by weight in the treatment fluids of the present invention. Depending on the temperature and porosity of the subterranean formation being treated, these concentrations of the relative permeability modifier can be ineffective to produce a water permeability reduction of greater than about 80% in the absence of a companion polymer. Alternately, these concentrations of relative permeability modifier may produce an aqueous fluid injection pressure increase of about 20 psi [about 140 kPa] or greater, about 100 psi [about 690 kPa] or greater, or about 300 psi [about 2100 kPa] or greater.

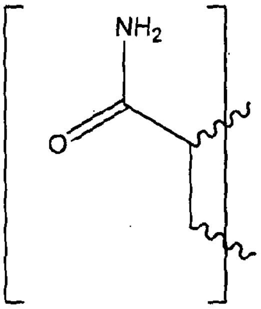
[0070] The concentration of the companion polymer in the present treatment fluids is generally chosen such that the water permeability is less than about 80% or the aqueous fluid injection pressure increase is less than about 100 psi [about 690 kPa] when a subterranean formation is treated using the companion polymer alone. Although not required to be so, a concentration of the companion polymer is generally less than the concentration of the relative permeability modifier. The total polymer concentration (*e.g.*, the aggregate concentration of relative permeability modifier and companion polymer) may be less than the relative permeability modifier concentrations used in conventional treatment fluids of the art. Concentrations of the companion polymer are generally about 0.25% or below by weight in the treatment fluids of the present invention. A concentration of the companion polymer may be about 0.2% or below by weight in the treatment fluid, or about 0.15% or below by weight in the treatment fluid, or about 0.1% or below by weight in the treatment fluid, or about 0.05% or below by weight in the treatment fluid, or about 0.04% or below by weight in the treatment fluid, or about 0.03% or below by weight in the treatment fluid, or about 0.02% or below by weight in the treatment fluid, or about 0.01% or below by weight in the treatment fluids. A concentration of the companion polymer may range between about 0.25% and 0.005% by weight in the treatment fluid. A concentration of the companion polymer may range between about 0.025% and about 0.0075% by weight in the treatment fluid.

[0071] A number of different companion polymers may be used in the present invention, whereby synergistic interactions with a relative permeability modifier can be observed in a treatment fluid. The companion polymer may not be a hydrophobically modified polymer. The companion polymer may comprise at least one of a cationic, an anionic or a non-ionic polymer. The companion polymer may comprise at least one of an acrylamide monomer unit or an acrylate ester monomer unit. That is, the companion polymer may be a polyacrylamide, a polyacrylate, or an acrylate/acrylamide copolymer. Suitable companion polymers may also include acrylamide/diallyldimethyl ammonium chloride copolymers, diutans, and polyethyleneimine. A suitable polyethyleneimine for use in the present invention may be "HZ-20," which is commercially available from Halliburton Energy Services of Duncan, Oklahoma.

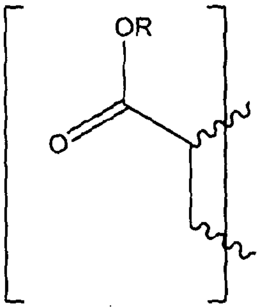
[0072] Diutans are polysaccharide structures that often have a gum-like consistency. The use of diutans in treatment fluids are described in commonly owned United States Patents 7,445,044; 7,547,665; 7,584,791; 7,595,282; 7,621,334; 7,694,739; 7,717,180;

7,727,936; 7,727,937; 7,748,456; 7,814,980; 7,829,508; 7,846,877; 7,862,655; and 7,883,944, each of which is incorporated herein by reference in its entirety. The diutan may be a clarified diutan.

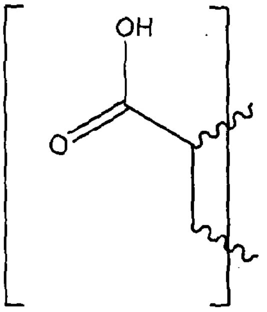
[0073] The companion polymer may contain a repeat unit derived from acrylamide. A portion of a companion polymer containing an acrylamide repeat unit is shown below, where the wavy lines represent bonding to other monomer units.



The companion polymer may be a polyacrylate. A portion of a companion polymer containing an acrylate ester repeat unit is shown below, where the wavy lines represent bonding to other monomer units and R is an alkyl or aryl group, for example.



At least a portion of the side chains of the companion polymer may be hydrolyzed. That is, when the companion polymer contains acrylamide and/or acrylate ester repeat units, at least a portion of the side chain amide or carboxylic esters therein may be hydrolyzed to the corresponding carboxylic acid. In such embodiments in which at least a portion of the side chains are hydrolyzed, at least a portion of the companion polymer may contain acrylic acid monomer units. A partial structure of a companion polymer containing acrylic acid monomer units is shown below, where the wavy lines represent bonding to other monomer units (*e.g.*, other acrylic acid monomer units and/or other acrylamide or acrylate ester monomer units).



Depending on the pH, companion polymers having hydrolyzed side chains can be in their protonated (*i.e.*, acidic) or deprotonated (*i.e.*, anionic forms).

[0074] The companion polymer may be a polyacrylamide, specifically a polyacrylamide in which at least a portion of the side chains are hydrolyzed. A number of partially hydrolyzed polyacrylamides are known in the art and commercially available. Two commercially available polyacrylamides that are suitable for use in the present invention include, for example, "FR-66" and "FDP-835," each of which is available from Halliburton Energy Services of Duncan, Oklahoma. "FR-66" is a partially hydrolyzed polyacrylamide available in an oil base having a molecular weight of at least about 10,000,000. "FDP-835" is a partially hydrolyzed polyacrylamide available in an aqueous solution having a molecular weight of less than about 500,000. Hence, the molecular weight of the companion polymer may span a wide range. A molecular weight of the polyacrylamide may range between about 100,000 and about 10,000,000 or between about 500,000 and about 10,000,000. Higher or lower molecular weights for a polyacrylamide companion polymer can also be suitable and lie within the scope of the present invention.

[0075] The companion polymer may have at least some propensity for modifying the water permeability of a subterranean formation. This is particularly true for partially hydrolyzed polyacrylamides, which may be used as the companion polymer in the present invention. At the concentrations used in the present invention, however, these companion polymers do not typically achieve a reduction in water permeability of greater than about 80% without the relative permeability modifier being present. As noted above, there can be a synergistic interaction between the relative permeability modifier and the companion polymer such that the propensity of the present treatment fluids for modifying the water permeability or the aqueous fluid injection pressure of a subterranean formation is greater than the additive effect of the relative permeability modifier and the companion polymer, each acting independently. Without being limited by theory or mechanism, the companion polymer can increase the water permeability reduction exerted by the relative permeability modifier and/or the relative permeability modifier can increase the water permeability reduction exerted by the companion polymer, particularly when the companion polymer itself has significant water permeability reduction properties.

[0076] In general, it is desirable to hold the total polymer concentration as low as possible. For example, excessive concentrations of polyacrylamide or partially hydrolyzed polyacrylamides in a subterranean formation can result in an unacceptable reduction in hydrocarbon production therefrom. By keeping the concentration of a polyacrylamide companion polymer as small as possible, this problem can be minimized. The same can hold true for "HPT-1" and other relative permeability modifiers. That is, excessive amounts of relative permeability modifier can detrimentally impact the subterranean formation's permeability to hydrocarbons in some embodiments.

[0077] The treatment fluids of the present invention may further comprise at least one surfactant. Such surfactants include cationic surfactants, anionic surfactants, zwitterionic surfactants and non-ionic surfactants, numerous examples of each of which are known to one of ordinary skill in the art. When present, a surfactant may be used in the present treatment fluids at a concentration ranging between about 0.1% and about 2.0% by weight or between about 0.5% and about 1.0%.

[0078] Illustrative examples of surfactants can include, without limitation, ethoxylated nonyl phenol phosphate esters, alkyl phosphonates, linear alcohols, nonylphenol compounds, alkyoxylated fatty acids, alkylphenol alkoxylates, ethoxylated amides, ethoxylated alkyl amines, betaines, methyl ester sulfonates (*e.g.*, as described in commonly owned United States Patents 7,159,659; 7,299,874; and 7,303,019 and United States Patent Application 11/058,611, filed February 2, 2005 (now available as United States Patent Application Publication 2006/0183646), the entire disclosures of which are incorporated herein by reference), hydrolyzed keratin (*e.g.*, as described in commonly owned United States Patent No. 6,547,871, the entire disclosure of which is incorporated herein by reference), sulfosuccinates, taurates, amine oxides, alkoxylated fatty acids, alkoxylated alcohols (*e.g.*, lauryl alcohol ethoxylate, ethoxylated nonyl phenol), ethoxylated fatty amines, ethoxylated alkyl amines (*e.g.*, cocoalkylamine ethoxylate), modified betaines, alkylamidobetaines (*e.g.*, cocoamidopropyl betaine) and quaternary ammonium compounds (*e.g.*, trimethyltallowammonium chloride, trimethylcocoammonium chloride). Suitable surfactants can be used in a liquid or powder form.

[0079] The at least one surfactant may be selected such that it improves the stability of the treatment fluid by inhibiting or substantially minimizing precipitation that can occur for some relative permeability modifiers at high pH and/or elevated temperature. Co-pending and commonly owned United States Patent Application 12/956,569, filed November 30, 2010, which is incorporated herein by reference in its entirety, provides further disclosure to this effect.

[0080] The present treatment fluids may further include at least one anionic surfactant that improves their stability. Suitable anionic surfactants that can improve the stability of the present treatment fluid include, for example, poly(ethylene oxide) sulfonates, poly(ethylene oxide) carboxylates, poly(ethylene oxide) sulfates, poly(propylene oxide) sulfonates, poly(propylene oxide) carboxylates and poly(propylene oxide) sulfates. Particularly suitable anionic surfactants can include, for example, "EMULSOGEN COL 100" and "EMULSOGEN LS 24N," each of which is a poly(ethylene oxide) anionic surfactant that is available from Clariant Corporation, and "EMCOL CNP 110," a poly(ethylene oxide) anionic surfactant that is available from Akzo Nobel Corporation.

[0081] The present treatment fluids may include at least one surfactant that is not an anionic surfactant, which can optionally be used in combination with an anionic surfactant. Suitable surfactants may be amphoteric surfactants such as, for example, fatty acids having quaternized amine groups, betaines (*e.g.*, cocoamidopropyl betaine, palmitamidopropyl betaine and lauryl betaine), glycinates and imidazolines. A suitable amphoteric surfactant may be "HC-2," an amphoteric surfactant that is commercially available from Halliburton Energy Services of Duncan, Oklahoma.

[0082] Further, the present treatment fluids can optionally comprise any number of additional additives commonly used in treatment fluids including, for example, scale inhibitors, corrosion inhibitors, gelling agents, crosslinking agents, foaming agents, defoaming agents, antifoam agents, emulsifying agents, de-emulsifying agents, iron control agents, proppants or other particulates, particulate diverters, salts, acids, fluid loss control additives, gas, catalysts, clay control agents, dispersants, flocculants, scavengers (*e.g.*, H_2S scavengers, CO_2 scavengers or O_2 scavengers), lubricants, breakers, friction reducers, bridging agents, viscosifiers, weighting agents, solubilizers, pH control agents (*e.g.*, buffers), hydrate inhibitors, consolidating agents, bactericides, and the like. Combinations of these additives can be used as well.

[0083] The present compositions and methods may reduce the permeability of at least a portion of a subterranean formation to aqueous based fluids without substantially changing the permeability of the subterranean formation to hydrocarbons. After placement downhole in a subterranean formation containing water-producing zones and hydrocarbon-producing zones, the relative permeability modifier alters the permeability of the water-producing zones without substantially affecting the production of hydrocarbons from the hydrocarbon-producing zones. Without being bound by theory or mechanism, it is believed that during normal "leak-off" of the base fluid of the treatment fluid, the relative permeability modifier is adsorbed into the subterranean formation, thereby leading to a significant reduction in water permeability. It will be appreciated by one of ordinary skill in the art that the present compositions and methods are advantageous, at a minimum, because they allow zonal isolation between the water-producing zones and the hydrocarbon-producing zones of a subterranean formation at the time of completion, thereby eliminating or postponing the need for water shutoff during the production phase of the well. Further, the present compositions and methods can advantageously extend the life of a well. Treatment fluids of the present invention can be used in both newly drilled subterranean formations and in formations needing re-stimulation.

[0084] To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

EXAMPLES

[0085] Example 1: Brine Permeability in Brown Sandstone at 175°F [79.4°C]. A sandstone core was treated with a treatment fluid containing a relative permeability modifier and various polyacrylamide-based companion polymers at the concentrations indicated in Table 1. Permeability measurements were made at 175°F [79.4°C]. The base fluid of the treatment fluid was 2% aqueous KCl. The reduction in core permeability was measured according to standard methods described in United States Patent 6,476,169, which is incorporated herein by reference in its entirety above. The sequence of addition for the permeability measurements was 1) water, 2) oil, 3) water, 4) treatment fluid, and 5) water. Testing results demonstrating a synergistic effect are summarized in Table 1.

Table 1

Treatment Fluid Composition	Treatment Fluid Concentration (wt. %)	Treatment Volume (mL)	Total Amount of Polymer (g)	Pressure Increase After Treatment (psi) [kPa]	Permeability Reduction (%)
HPT-1	0.060	150	0.09	8 [55]	44
FR-66[b]	0.025	150	0.0375	30 [210]	69
HPT-1/ FR-66	0.060/ 0.025	150	0.09/ 0.0375	69 [480]	99
HPT-1/ FDP-835[c]	0.060/ 0.025	100	0.06/ 0.025	500 [3400]	98

[a] "HPT-1" is a hydrophobically modified hydrophilic polymer that is available from Halliburton Energy Services of Duncan, Oklahoma.
[b] "FR-66" is a partially hydrolyzed polyacrylamide emulsion in oil having a molecular weight of greater than about 10,000,000 that is available from Halliburton Energy Services of Duncan, Oklahoma.
[c] "FDP-835" is a partially hydrolyzed polyacrylamide aqueous solution having a molecular weight of less than about 500,000 that is available from Halliburton Energy Services of Duncan, Oklahoma.

[0086] The results in Table 1 demonstrate the synergistic interactions between polyacrylamide companion polymers and a hydrophobically modified hydrophilic polymer relative permeability modifier. When "FR-66" and "HPT-1" were used separately for treatment, poor water permeability reduction was observed. However, when mixed together at like concentrations in a treatment fluid, a very high water permeability reduction and a non-additive injection pressure increase were observed. Similar effects were observed for the combination of “HPT-1” and “FDP-835.” It should be noted that the treatment fluid containing “FDP-835” produced a greater injection pressure increase than did “FR-66” in spite of its lower molecular weight. The difference in injection pressure increase may possibly be attributed to the oil emulsion of “FR-66” or differences in the hydrolysis levels of the two companion polymers.

[0087] Example 2: Brine Permeability in Oklahoma #1 Sand Pack at Room Temperature. Permeability testing was conducted as described above for Example 1, except the core sample was an Oklahoma #1 Sand Pack and testing was conducted at room temperature. In this case the sequence of addition for the water permeability measurements was 1) water, 2) treatment fluid, and 3) water. Testing results demonstrating a synergistic effect are summarized in Table 2.

Table 2

Treatment Fluid Composition	Treatment Fluid Concentration (wt. %)	Treatment Volume (mL)	Total Amount of Polymer (g)	Pressure Increase After Treatment (psi) [kPa]	Permeability Reduction (%)
HPT-1	0.12	150	0.18	1.3 [9]	13
FR-66	0.025	150	0.0375	97 [670]	67
HPT-1/ FR-66	0.12/ 0.025	42	0.05/ 0.0105	500 [3400]	99
HPT-1	0.12	150	0.18	1.3 [9]	13
FR-48[d]	0.025	150	0.0375	32 [220]	60
HPT-1/ FR-48	0.12/ 0.025	86	0.103/ 0.0215	500 [3400]	98
HPT-1	0.12	150	0.18	1.3 [9]	13
FDP-835	0.2	150	0.3	3 [21]	3
HPT-1/ FDP-835	0.12/ 0.2	117	0.14/ 0.23	500 [3400]	99

[d] “FR-48” is an acrylamide/diallyldimethylammonium chloride copolymer that is available from Halliburton Energy Services of Duncan, Oklahoma.

[0088] In this example, synergistic interactions were again observed between a polyacrylamide companion polymer and a hydrophobically modified hydrophilic polymer for reducing the water permeability and increasing the injection pressure of a sand pack, much like that shown in Example 1. In all cases shown in Table 2, the combination of "HPT-1" and the companion polymer exerted a water permeability reduction that was greater than the additive amount of permeability reduction of the "HPT-1" and the companion polymer acting independently. The same was true for the injection pressure increase, where the increase was greater than the amount obtained from the individual polymer solutions.

[0089] Testing was also conducted in Oklahoma #1 Sand Pack where the "HPT-1" and the companion polymer ("FR-66") were added *sequentially rather than combined in a* single treatment fluid. In this case, much poorer water permeability reduction was observed. Testing results for sequential addition are summarized in Table 3.

Table 3

Treatment Fluid Composition	Treatment Fluid Concentration (wt. %)	Treatment Volume (mL)	Pressure Increase After Treatment (psi) [kPa]	Permeability Reduction (%)
Stage 1: HPT-1	0.12	150	3 [21]	n/d
Stage 2: FR-66	0.025	150	4 [28]	n/d

Total Permeability Reduction = 18%

The low pressure increase observed after the "FR-66" stage is particularly surprising, since this companion polymer produced a 66 psi pressure increase alone (see Table 2). This data further illustrates that when the relative permeability modifier and the companion polymer are combined in a treatment fluid, there is a synergistic interaction between the polymers.

[0090] Example 3: Brine Permeability in Oklahoma #1 Sand Pack Column #2 (96% Oklahoma #1 Sand, 2% Bentonite and 2% Silica Flour) at Room Temperature. Permeability testing was conducted as described above for Example 1, except the sample was a mixture of Oklahoma #1 Sand (96%), Bentonite (2%) and silica flour (2%), and testing was conducted at room temperature. In this case the sequence of addition for the water permeability measurements was 1) water, 2) treatment fluid, and 3) water. Testing results demonstrating a synergistic effect are summarized in Table 4.

Table 4

Treatment Fluid Composition	Treatment Fluid Concentration (wt. %)	Treatment Volume (mL)	Total Amount of Polymer (g)	Pressure Increase After Treatment (psi) [kPa]	Permeability Reduction (%)
HPT-1	0.060	150	0.09	11 [76]	56
Diutan	0.025	150	0.0375	85 [590]	68
HPT-1/ Diutan	0.060/ 0.025	150	0.09/ 0.0375	414 [2900]	97
HPT-1	0.060	150	0.09	11 [76]	56
HZ-20[e]	0.025	150	0.0375	62 [430]	78
HPT-1/ HZ-20	0.060/ 0.025	88	0.06/ 0.025	500 [3400]	99

[e] "HZ-20" is a polyethyleneimine that is available from Halliburton Energy Services of Duncan, Oklahoma.

In this example, like polymer concentrations produced a water permeability reduction and injection pressure increase that were significantly higher for the synergistic combination of "HPT-1" and companion polymer. Synergistic interactions were observed at low "HPT-1" concentrations with a non-ionic polymer (diutan) and polyethyleneimine, a cationic polyamine. Such reductions of the relative permeability modifier quantities can result in significant cost savings for treatment operations.

[0091] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to one skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope of the present invention. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS:

1. A method comprising:

providing a treatment fluid that comprises:

a base fluid;

a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and

a companion polymer that comprises at least an acrylamide monomer unit;

wherein the companion polymer is not hydrophobically modified; and

placing the treatment fluid in at least a portion of a subterranean formation.

2. A method according to claim 1, wherein the method further comprises allowing the treatment fluid to reduce a water permeability or to increase an aqueous fluid injection pressure of the portion of the subterranean formation.

3. A method comprising:

providing a treatment fluid that comprises:

a base fluid;

a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and

a companion polymer interacting synergistically with the relative permeability modifier such that the treatment fluid is operable to reduce the water permeability or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation by more than through using the relative permeability modifier or the companion polymer acting alone at like concentration; and

placing the treatment fluid in at least a portion of a subterranean formation.

4. A method according to any one of the preceding claims, wherein the hydrophobically modified hydrophilic polymer comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

5. A method comprising:

providing a treatment fluid that comprises:

a base fluid;

a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer comprising at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide;

wherein a concentration of the relative permeability modifier in the treatment fluid is below its normal effective working concentration; and

a companion polymer; and

wherein the treatment fluid is operable to reduce the water permeability of at least a portion of a subterranean formation by at least about 80% or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation above about 100 psi [about 690kPa]; and

placing the treatment fluid in at least a portion of a subterranean formation.

6. A method according to claim 3 or claim 5, wherein the companion polymer is not hydrophobically modified.

7. A method according to any one of the preceding claims, wherein the treatment fluid is operable to reduce the water permeability of the portion of the subterranean formation by at least about 80%; and

wherein a concentration of the relative permeability modifier in the treatment fluid is only operable to reduce the water permeability of the portion of the subterranean formation by about 5% to about 80% without the companion polymer.

8. A method according to any one of the preceding claims, wherein the treatment fluid is operable to reduce the water permeability of the portion of the subterranean formation by more than an additive water permeability reduction or to increase the aqueous fluid injection pressure of the portion of the subterranean formation by more than an additive aqueous fluid injection pressure increase obtained from the relative permeability modifier and the companion polymer, each acting independently.

9. A method according to any one of the preceding claims, wherein the companion polymer comprises at least one of a cationic, an anionic or a non-ionic polymer.

10. A method according to any one of the preceding claims, wherein the companion polymer comprises at least one polymer selected from the group consisting of a polyacrylate, a polyacrylamide, an acrylate/acrylamide copolymer, and an acrylamide/diallyldimethylammonium chloride copolymer.

11. A method according to any one of the preceding claims, wherein at least a portion of the side chains of the companion polymer are hydrolyzed.

12. A method according to any one of the preceding claims, wherein the companion polymer comprises at least one of an acrylamide monomer unit or an acrylate ester monomer unit.

13. A method according to claim 3 or claim 5 or claim 6, wherein the companion polymer comprises at least one polymer selected from the group consisting of a diutan and polyethylenimine.

14. A treatment fluid comprising:

a base fluid;

a relative permeability modifier that comprises a hydrophobically modified hydrophilic polymer; and

a companion polymer interacting synergistically with the relative permeability modifier such that the treatment fluid is operable to reduce the water permeability or to increase an aqueous fluid injection pressure of at least a portion of a subterranean formation by more than through using the relative permeability modifier or the companion polymer acting alone.

15. A treatment fluid according to claim 14, wherein the companion polymer is not hydrophobically modified.

16. A treatment fluid according to any one of claims 13 to 15, wherein the hydrophobically modified hydrophilic polymer comprises at least one monomer unit derived from a cetyldimethylammoniumethyl methacrylate halide.

17. A treatment fluid according to any one of claims 14 to 16, wherein the companion polymer comprises at least one of a cationic, an anionic or a non-ionic polymer.

18. A treatment fluid according to any one of claims 14 to 17, wherein the companion polymer comprises at least one polymer selected from the group consisting of a polyacrylate, a polyacrylamide, an acrylate/acrylamide copolymer, an acrylamide/diallyldimethylammonium chloride copolymer, a diutan, and polyethylenimine.

19. A treatment fluid according to any one of claims 14 to 18, wherein the companion polymer comprises at least one of an acrylamide monomer unit or an acrylate ester monomer unit.

20. A treatment fluid according to any one of claims 14 to 18, wherein the companion polymer comprises at least one polymer selected from the group consisting of a diutan and polyethylenimine.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/000315

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/035 C09K8/508 C09K8/588
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/095535 A1 (NGUYEN PHILIP D [US]) 16 April 2009 (2009-04-16) abstract paragraphs [0053], [0086] the whole document -----	1-12, 14-19
X	US 2006/124309 A1 (NGUYEN PHILIP D [US] ET AL) 15 June 2006 (2006-06-15) paragraphs [0009], [0022], [0026], [0038], [0070], [0092] the whole document -----	1-12, 14-19
X	WO 2008/096165 A1 (HALLIBURTON ENERGY SERV INC [US]; CURTIS PHILIP ANTHONY [GB]; ROBB IAN) 14 August 2008 (2008-08-14) paragraphs [0039], [0041], [0042] the whole document ----- -/--	3-10, 13-18,20

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

☒ See patent family annex.

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 19 June 2012	Date of mailing of the international search report 27/06/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Straub, Thomas

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/000315

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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		WO 2009125164 A1	15-10-2009