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(54) **Title:** DEGRADABLE FLUID SEALING COMPOSITIONS HAVING AN ADJUSTABLE DEGRADATION RATE AND METHODS FOR USE THEREOF

(57) **Abstract:** When performing subterranean treatment operations, it can be desirable to temporarily divert or block fluid flow by forming a degradable fluid seal. Methods for forming a degradable fluid seal can comprise: providing a sealing composition comprising: a degradable polymer, and a water-soluble material comprising a first portion and a second portion of rigid particulates, each portion having a sealing time and a particulate size distribution associated therewith, the particulate size distributions of the first portion and the second portion differing from one another; determining an amount of the first portion relative to the second portion needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the first portion or the second portion; introducing the sealing composition into a subterranean formation; and allowing the sealing composition to form a degradable fluid seal in the subterranean formation.



## DEGRADABLE FLUID SEALING COMPOSITIONS HAVING AN ADJUSTABLE DEGRADATION RATE AND METHODS FOR USE THEREOF

### BACKGROUND

[0001] The present disclosure relates to methods and compositions for fluid blocking and diversion in subterranean formations, and, more specifically, to treatment operations that form a temporary fluid seal in a subterranean formation.

[0002] Treatment fluids can be used in a variety of subterranean operations. Such subterranean operations can include, without limitation, drilling operations, stimulation operations, production operations, remediation operations, sand control treatments and the like. As used herein, the terms "treat," "treatment," and "treating" refer to any subterranean operation that uses a fluid in conjunction with achieving a desired function and/or for a desired purpose. Use of these terms does not imply any particular action by the treatment fluid. Illustrative treatment operations can include, for example, fracturing operations, gravel packing operations, acidizing treatments, scale dissolution and removal, consolidation treatments, and the like.

[0003] When performing these or other subterranean treatment operations, it can sometimes be desirable to temporarily or permanently block or divert the flow of a fluid within at least a portion of the subterranean formation. The blocking or diversion of the fluid can itself be considered a treatment operation. Illustrative fluid blocking and diversion operations can include, without limitation, fluid loss control operations, kill operations, conformance control operations, and the like. The fluid that is blocked or diverted can be a formation fluid that is natively present in the subterranean formation, such as petroleum, gas, or water. In other cases, the fluid that is blocked or diverted can be a subterranean treatment fluid, including the types mentioned above. In some cases, treatment fluids can be made to be self-diverting, such that they are directed to a desired location within the subterranean formation.

[0004] Providing effective fluid loss control during subterranean treatment operations can be highly desirable. "Fluid loss," as used herein, refers to the undesired migration or loss of fluids into a subterranean formation and/or a particulate pack. Fluid loss can be problematic in a number of subterranean operations including, for example, drilling operations, fracturing operations, acidizing operations, gravel-packing operations, workover operations, chemical

treatment operations, wellbore clean-out operations, and the like. In fracturing operations, for example, fluid loss into the formation matrix can sometimes result in incomplete fracture propagation.

5       **[0005]** Diverting agents can function similarly to fluid loss control agents, but may involve a somewhat different approach. Diverting agents can be used to seal off a portion of the subterranean formation. By sealing off a portion of the subterranean formation, a treatment fluid can be diverted from a highly permeable portion of the subterranean formation to a lower permeability portion, for example. Plugging or sealing agents can be used similarly to  
10       diverting agents, except they are generally used to seal off the wellbore to provide zonal isolation.

**[0006]** When only a temporary blocking or diversion of fluid is desired, a fluid seal within a subterranean formation can be removed to allow fluid flow to resume. In some cases, an external degradant can be introduced to the  
15       subterranean formation to remove the fluid seal. The external degradant agent may be introduced to the subterranean formation after the fluid seal is no longer necessary (*e.g.*, after performing a treatment operation). Use of an external degradant in a separate cleanup operation can add to the time and expense needed to produce a fluid from the subterranean formation. In other cases, a  
20       fluid seal may comprise a substance that is natively unstable, such that the fluid seal degrades and/or dissolves over time to allow fluid flow to resume. When relying on the native degradation rate of a fluid seal, undesirably slow degradation can again add to the time and expense of production operations.

**[0007]** Gelled polymers can be used to form a fluid seal in subterranean  
25       operations. As used herein, a "gelled polymer" refers to a polymer in semi-solid form that has at least a portion of its polymer chains crosslinked with one another via a crosslinking agent. A gelled polymer has a rheological yield point. It is to be understood in the description that follows that any reference to a gelled polymer refers to a polymer that is crosslinked. Crosslinked  
30       polyacrylamide, other acrylamide-containing polymers, and hydrolyzed or partially hydrolyzed variants thereof are illustrative examples of gelled polymers that can be used in subterranean operations.

**[0008]** Various modes of crosslinking can be used to form the crosslinks in a gelled polymer. The crosslinks can be in the form of a covalent bond or a  
35       non-covalent bonding interaction. They can be temporary or permanent.

Chromium and other transition metal ions can be used to crosslink acrylamide-containing polymers. Polymer gels formed using such crosslinking agents have proven unsuitable at higher temperatures (*e.g.*, above about 80°C) due to uncontrolled crosslinking rates (*e.g.*, short gel-times), crosslinking agent precipitation, polymer degradation, and the like. In addition, chromium and certain other transition metal ions can have an undesirable environmental impact. Acrylamide-containing polymers can also be crosslinked with polyalkyleneimines and polyalkylenepolyamines. Depending on the type and concentration of crosslinking agent used, the gel-times and gel strengths of the gelled polymers can be impacted.

**[0009]** Gelled acrylamide-containing polymers can be particularly effective for fluid blocking and diversion in lower permeability formations (*e.g.*, formations having a permeability of about 0.1 darcy (D) or lower). As the formation permeability increases, gelled acrylamide-containing polymers can become less effective due to their reduced ability to block larger pore throats that can be characteristic of higher permeability formations. For example, above about 0.1 D, and particularly above about 0.5 D, gelled acrylamide-containing polymers may be less effective for blocking or diverting fluid flow at normal formation operating temperatures and pressures. To block these larger pore throats in higher permeability formations, particulate matter may be added to gelled acrylamide-containing polymers as a bridging agent.

### SUMMARY OF THE INVENTION

**[0010]** The present disclosure relates to methods and compositions for fluid blocking and diversion in subterranean formations, and, more specifically, to treatment operations that form a temporary fluid seal in a subterranean formation.

**[0011]** In some embodiments, the present disclosure provides a method comprising: providing a sealing composition comprising: a degradable polymer, and a water-soluble material comprising a first portion of rigid particulates and a second portion of rigid particulates, each portion of rigid particulates having a sealing time and a particulate size distribution associated therewith, the particulate size distributions of the first portion of rigid particulates and the second portion of rigid particulates differing from one another; determining an amount of the first portion of rigid particulates relative to the second portion of

rigid particulates in the sealing composition needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the first portion of rigid particulates or the second portion of rigid particulates; introducing the sealing composition into a subterranean formation; and allowing the sealing composition to form a degradable fluid seal in the subterranean formation.

**[0012]** In other embodiments, the present disclosure provides a method comprising: providing a sealing composition comprising: particulates of a gelled degradable polymer, and a water-soluble material comprising rigid particulates having a sealing time and a particulate size distribution associated therewith, the particulate size distribution of the water-soluble material differing from that of a like unsized water-soluble material; determining a particulate size distribution of the rigid particulates needed to produce a degradable fluid seal having a desired sealing time; introducing the sealing composition into a subterranean formation; forming a degradable fluid seal in the subterranean formation from the sealing composition; performing a treatment operation in the subterranean formation while the degradable fluid seal is intact; and allowing the degradable fluid seal to degrade.

**[0013]** In still other embodiments, the present disclosure provides a method comprising: providing a plurality of gelled degradable polymer particulates; providing a first portion of a water-soluble material and a second portion of a water-soluble material, each portion comprising rigid particulates and each portion having a sealing time and a particulate size distribution associated therewith, the particulate size distributions differing from one another; mixing the first portion of the water-soluble material and the second portion of the water-soluble material with the plurality of gelled degradable polymer particulates, thereby forming a sealing composition; determining an amount of the first portion of the water-soluble material relative to the second portion of the water-soluble material in the sealing composition needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the first portion of the water-soluble material or the second portion of the water-soluble material; and introducing the sealing composition into a subterranean formation to form a degradable fluid seal therein.

[0014] The features and advantages of the present disclosure will be readily apparent to one having ordinary skill in the art upon a reading of the description of the preferred embodiments that follows.

### BRIEF DESCRIPTION OF THE DRAWINGS

5 [0015] The following figures are included to illustrate certain aspects of the present invention, and should not be viewed as exclusive embodiments. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to one having ordinary skill in the art and having the benefit of this disclosure.

10 [0016] FIGURE 1 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 14.3 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 85.7 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns.

15 [0017] FIGURE 2 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 18.6 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 81.4 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns.

20 [0018] FIGURE 3 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 21.4 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 78.6 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns.

25 [0019] FIGURE 4 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 28.6 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 71.4 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns.

### DETAILED DESCRIPTION

30 [0020] The present disclosure relates to methods and compositions for fluid blocking and diversion in subterranean formations, and, more specifically,

to treatment operations that form a temporary fluid seal in a subterranean formation.

**[0021]** As previously described, gelled degradable polymers can be used for fluid blocking and diversion in a subterranean formation. In low permeability formations, the gelled polymer alone may be suitable for this purpose. In higher permeability formations, however, particulates of a bridging agent may be used in combination with the gelled polymer so that wider pore throats in the formation can be sealed. The bridging agent particulates may comprise a rigid material. As used herein, the term "rigid" refers to a particulate form that is substantially non-pliable and substantially retains its shape when subjected to stress. Rigid particulates suitable for use in the present embodiments are described in more detail hereinafter.

**[0022]** Not only can rigid bridging particulates desirably facilitate the use of gelled polymers for fluid sealing and diversion applications in higher permeability subterranean formations, but the presence of the bridging particulates themselves may alter the degradation rate of a degradable fluid seal formed therefrom. In the case of crosslinked polyacrylamide as the gelled polymer and polyvinyl alcohol as the rigid bridging particulates, this result is particularly surprising, since an aqueous polyvinyl alcohol solution is non-buffering and produces a pH range (*e.g.*, ~5.5 - 7.5) that does not by itself appreciably impact the degradation rate of crosslinked polyacrylamide. Unless otherwise specified herein, a fluid seal will be considered to be degraded when it is no longer impermeable to a fluid of interest. After failure of the fluid seal, the seal may undergo further degradation and/or dissolution, as described hereinafter. A sealing time of the fluid seal may be a function of its degradation rate, which may be a function of, among other things, the degradation rate of the gelled polymer, the dissolution or degradation rate of the rigid bridging particulates, hydrophobicity or hydrophilicity of the rigid bridging particulates and/or the gelled polymer, pH and temperature conditions, and the presence of other materials that can accelerate or slow the degradation rate. As used herein the term "sealing time" refers to the period of time over which a seal is substantially impermeable to a fluid.

**[0023]** We have surprisingly discovered that the degradation rate of a fluid seal comprising a gelled degradable polymer can be further altered by using rigid bridging agent particulates that have a different particulate size distribution

than does a like unsized bridging agent. As used herein, the term "unsized" refers to the native particulate size distribution obtained when synthesizing a material. By sizing a sample of rigid bridging agent particulates, the degradation rate of a fluid seal formed therefrom can be desirably altered compared to that  
5 obtained using a comparable quantity of unsized rigid bridging agent particulates. Rigid bridging agent particulates having two or more different particulate size ranges can also be combined to create a custom particulate size distribution suitable for producing a desired degradation rate. By adjusting the relative amounts of the two or more different particulate size ranges relative to  
10 one another, the degradation rate of the fluid seal may be further altered. Although the use of rigid bridging agent particulates in a degradable fluid seal may be particularly advantageous in higher permeability subterranean formations (*e.g.*, about 0.5 D or greater), it is to be recognized that the foregoing benefits may also be realized in subterranean formations having a  
15 lower permeability.

**[0024]** The ability to alter the degradation rate of the fluid seal may be especially beneficial when it is desired to resume fluid flow or terminate fluid diversion before the native degradation of the fluid seal occurs. Further, by altering the degradation rate of the fluid seal from within, as opposed to using  
20 an external degradant in a cleanup fluid, the cost of goods can be minimized and lost time during cleanup operations can be avoided. Thus, by keeping the fluid seal intact only for as long as functionally necessary, the formation may be returned to production more quickly, thereby allowing beneficial cost savings to be realized.

**[0025]** More specifically, we have discovered that the combination of gelled degradable polymer particulates and rigid particulates of a water-soluble material may form degradable fluid seals whose degradation rate may be altered by varying the size distribution of the rigid particulates. As used herein, the term "water-soluble" refers to a material that is by itself water-soluble or  
30 becomes water-soluble upon undergoing a chemical transformation. No particular degree of water solubility is implied by the term "water-soluble." Degradable fluid seals formed from the combination of gelled degradable polymer particulates and rigid particulates of a water-soluble material may be particularly advantageous for subterranean operations, since the fluid seals may  
35 be self-cleaning. That is, the fluid seals are not believed to leave a residue



(damage) in the subterranean formation over the long term. Without being bound by theory or mechanism, it is believed that the degradable fluid seals described herein may begin to fail due to dissolution of the water-soluble material. Either concurrently with or subsequent to the dissolution of the water-soluble material, the degradable polymer particulates may degrade to form a substantially water-soluble material. Thus, both components of the degradable fluid seal may become soluble over time. It should be noted that the degradation of the gelled degradable polymer need not necessarily take place by chemical degradation. For example, in some cases, the degradation can take place by physical or enzymatic (biological) transformations. In some cases, the gelled degradable polymer may simply become soluble in a fluid or erode over time such that the seal is gradually removed. Unless otherwise specified herein, the mechanism by which the gelled degradable polymer degrades may take place in any manner. In the case of gelled polyacrylamide particulates, degradation may take place more rapidly at alkaline pH values, but there also may be a solubilization or erosion component to their degradation as well.

**[0026]** Particularly in embodiments in which gelled polyacrylamide particulates are used, further control over the degradation rate of the degradable fluid seal may be realized by adjusting the pH of a treatment fluid used to introduce the particulates into a subterranean formation. For example, if more rapid degradation of the degradable fluid seal is desired than can be realized through altering the size distribution of the water-soluble particulates, the pH of the treatment fluid may be increased. Specifically, in some embodiments, the pH of the treatment fluid may be raised using calcium carbonate or a comparable base, which may result in more rapid degradation of the polyacrylamide particulates. Conversely, in embodiments in which gelled polyacrylamide particulates are used, if slower degradation of the degradable fluid seal is desired, a treatment fluid having a lower pH may be used. Other types of materials may have different degradation characteristics. For example, esters may degrade more rapidly at either high or low pH, but degrade very slowly at intermediate pH (*e.g.*, a pH of about 3 to about 6). In some embodiments, particulates of calcium carbonate or a comparable base may be included in the degradable fluid seal, such that a localized alkaline environment is formed to promote degradation, particularly for a fluid seal comprising polyacrylamide particulates. In some embodiments, the base particulates can

comprise the water-soluble material. In other embodiments, base particulates can be used in conjunction with another water-soluble material that can be degraded with a base.

**[0027]** In various embodiments, sealing compositions described herein may comprise a degradable polymer and a water-soluble material comprising rigid particulates, where the size distribution of the water-soluble material differs from that of a like unsized water-soluble material. As used herein, a "like unsized water-soluble material" refers to a water-soluble material that has a substantially identical chemical composition, but a size distribution that differs from that of a sized water-soluble material. That is, a sized water-soluble material has a size distribution that measurably differs from that of an as-synthesized water-soluble material. In some embodiments, rigid particulates having two or more different particulate size ranges may be combined to form a water-soluble material having a particulate size distribution that differs from that of the comparable unsized water-soluble material. That is, in some embodiments, two or more portions of rigid particulates, each having particulate size distributions that differ from one another, may comprise the water-soluble material.

**[0028]** As one of ordinary skill in the art will recognize, there can be a distribution of particulate sizes in a material, where the particulate sizes may be clustered around a most likely value (*i.e.*, the mode value). In the absence of intervening factors, the distribution of particulate sizes may approximate a Gaussian distribution. However, as one of ordinary skill in the art will further recognize, the distribution of particulate sizes in a material is most often non-Gaussian, with the mode value being skewed to one side of the median value, often with a tail in the distribution curve favoring higher particulate sizes. Various techniques that will be familiar to one having ordinary skill in the art may be used to separate particulates having various size ranges from one another (*e.g.*, sieving). In general, sizing of the water-soluble material used in the present embodiments may take place through any particulate size separation technique, known or presently unknown.

**[0029]** When using sized particulates, the sized particulates may themselves have a distribution of particulate sizes. Particulates having two or more different particulate size ranges may be combined with one another to produce a sample having yet another particulate size distribution. In general,

when combining particulates having different particulate size ranges with one another, the resulting sample will have a different particulate size distribution than that of a like unsized material. Further, the particulate size distribution of the combined sample may be additionally altered by using different quantities of each sized particulate. In some embodiments, there may be two or more local maxima within the particulate size distribution of the combined sample. Two or more local maxima may be observed if the particulate size ranges are more separated from one another and/or if there are significant quantities of both particulate size ranges present in the combined sample. For example, the particulate size distribution of the combined sample may be bimodal, trimodal, or have a higher modality. In other embodiments, there may be a single maximum within the particulate size distribution of the combined sample. A single maximum may be observed in the combined sample of sized particulates if the particulate size ranges are closer to one another, particularly overlapping, and/or if there is a relatively small quantity of at least one of the particulates relative to the other. For example, the particulate size distribution plot of the combined sample may display a shoulder or like feature that is not present in the particulate size distribution plot of one of its components.

**[0030]** In some embodiments, the water-soluble material used herein may comprise at least two different particulate size ranges. Accordingly, the particulate size distribution of the water-soluble material may differ from that of a like unsized water-soluble material. In general, the combination of two or more different particulate size ranges of the water-soluble material may produce a particulate size distribution having any size or shape. In some embodiments, the particulate size distribution of the water-soluble material may have two or more local maxima. In other embodiments, the particulate size distribution of the water-soluble material may have a single maximum. In some embodiments, the particulate size distribution of the water-soluble material may differ measurably from the particulate size distribution of one or more of its components.

**[0031]** In some embodiments, the degradable polymer may comprise particulates of a gelled degradable polymer. In some embodiments, the degradable polymer may be crosslinked. For example, in some embodiments, the gelled degradable polymer may comprise at least one crosslinked polymer such as, for example, a crosslinked polyacrylamide, a crosslinked

polymethacrylamide, any hydrolyzed or partially hydrolyzed variant thereof, any copolymer thereof, any derivative thereof, and any combination thereof. As used herein, a partially hydrolyzed poly(meth)acrylamide will have at least a portion of its (meth)acrylamide monomer units hydrolyzed to (meth)acrylic acid.

5 Any partially hydrolyzed polymer variant that remains gellable may be used in the present embodiments. In some embodiments, between about 1% and about 30% of the (meth)acrylamide monomer units may be hydrolyzed. In alternative embodiments, non-particulate versions of these degradable polymers may be used as well. Techniques for preparing particulates of gelled polyacrylamide and  
10 other gellable polymers are described in detail in commonly owned United States Patent Application 13/190,509, filed July 26, 2011, which is incorporated herein by reference in its entirety. In some embodiments, the particulates may be produced by any combination of techniques including, for example, chopping; extruding through a die, a filter, or the like; high speed mixing; homogenizing;  
15 blending; emulsifying; and the like.

**[0032]** Examples of acrylamide- and methacrylamide-containing polymers suitable for use in the present embodiments are described in commonly owned United States Patent 6,176,315, which is incorporated herein by reference in its entirety. In some or other embodiments, suitable gelled  
20 degradable polymers may include stimuli-degradable gelled polymers such as those described in commonly owned United States Patent 7,306,040, which is incorporated herein by reference in its entirety.

**[0033]** In some embodiments, the gelled degradable polymers used herein may include ethylenically unsaturated monomers such as, for example,  
25 ionizable monomers (e.g., 1-N,N-diethylaminoethylmethacrylate, and the like); diallyldimethylammonium chloride; 2-acrylamido-2-methyl propane sulfonate; acrylic acid; allylic monomers (e.g., diallyl phthalate; diallyl maleate; allyldiglycol carbonate; and the like); vinyl formate; vinyl acetate; vinyl propionate; vinyl butyrate; crotonic acid; itaconic acid; acrylamide;  
30 methacrylamide; methacrylonitrile; acrolein; methyl vinyl ether; ethyl vinyl ether; vinyl ketone; ethyl vinyl ketone; allyl acetate; allyl propionate; diethyl maleate; any derivative thereof; and any copolymer thereof.

**[0034]** In some embodiments, a crosslinking agent used to form the gelled degradable polymer may comprise an organic crosslinking agent. In some  
35 embodiments, the degradation rate of the gelled degradable polymer may be

altered by changing the identity and/or concentration of the crosslinking agent. Accordingly, the degradation rate of the degradable fluid seal may be further adjusted by altering the identity and/or concentration of the crosslinking agent in the gelled degradable polymer. In some embodiments, the crosslinking agent itself may be degradable. Suitable degradable crosslinking agents may comprise degradable functional groups such as, for example, esters, phosphate esters, amides, acetals, ketals, orthoesters, carbonates, anhydrides, silyl ethers, alkene oxides, ethers, imines, ether esters, ester amides, ester urethanes, carbonate urethanes, amino acids, any derivative thereof, or any combination thereof. The choice of the degradable functional group(s) used in the degradable crosslinking agent may be determined by the pH and temperature conditions under which the degradable fluid seal will be used, for example.

**[0035]** The size of the gelled degradable polymer particulates is not believed to be particularly limited. In some embodiments, the gelled degradable polymer particulates may range between about 1 micron and about 10 mm in size. In other embodiments, the gelled degradable polymer particulates may range between about 10 microns and about 1 mm in size. In still other embodiments, the gelled degradable polymer particulates may range between about 50 microns and about 500 microns in size. In some embodiments, the gelled degradable polymer particulates may be at least about 50 microns in size, or at least about 100 microns in size in other embodiments.

**[0036]** In general, rigid particulates of any water-soluble material may be used in the present embodiments. Both inorganic and organic water-soluble materials may be used. The rigid particulates are not particularly limited in shape, which may include various non-limiting forms such as, for example, platelets, shavings, flakes, ribbons, rods, strips, spheroids, toroids, pellets, tablets, needles, powders and/or the like. The choice of a suitable water-soluble material may be dictated by operational needs including, for example, dissolution rate, subterranean formation temperature and pH, availability of different particulate size ranges, chemical compatibility, environmental concerns, and the like. For example, if the water solubility of the water-soluble material is too great, premature failure of the degradable fluid seal may occur. Likewise, if the water solubility is too low, the water-soluble material may not sufficiently alter the degradation rate of the degradable fluid seal over that of its native degradation rate, even if sized particulates are used.

**[0037]** In some embodiments, a suitable water-soluble material may comprise a water-soluble polymer. Water-soluble polymers that may form rigid particulates may include, for example, polyvinyl alcohol, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, carboxyethyl cellulose, acetyl cellulose, hydroxyethyl cellulose, shellac, chitosan, chitin, dextran, guar, xanthan, starch, scleroglucans, a diutan, poly(vinyl pyrrolidone), polyacrylamide, polyacrylic acid, poly(diallyldimethylammonium chloride), poly(ethylene glycol), poly(ethylene oxide), polylysine, polymethacrylamide, polymethacrylic acid, poly(vinylamine), any derivative thereof, any copolymer thereof, and any combination thereof. In some embodiments, the foregoing polymers may be crosslinked to alter their dissolution rate and/or their hydrophobicity. Crosslinking may also improve the rigidity of particulates formed therefrom. In other embodiments, fish eyes may be formed from the foregoing polymers to alter their dissolution rate. Derivatization and the degree of functionalization may also impact the water solubility and polymer dissolution rate in some cases. In some embodiments, the polymer may not become water soluble until after hydrolysis of at least a portion of its functional groups. This behavior may be seen in methyl cellulose, ethyl cellulose, and acetyl cellulose, for example.

**[0038]** In some embodiments, the water-soluble material may comprise polyvinyl alcohol. Polyvinyl alcohol may be particularly advantageous for use in the present embodiments. Polyvinyl alcohol may be produced by at least partial hydrolysis of polyvinyl acetate or a like acylated polymer. In some or other embodiments, polyvinyl acetate having a sufficient degree of hydrolysis to be at least partially water soluble may be used. A chief advantage of polyvinyl alcohol for use in the present embodiments is that it is non-toxic and biodegradable, which facilitates its use in the medical and textile industries, for example. Polyvinyl alcohol may be obtained in many forms including, for example, fibers, sheets, granules, beads, powders, and the like. Further, polyvinyl alcohol may exist as an amorphous solid in an aqueous environment or become completely soluble depending upon the solution conditions. Among factors that can affect the dissolution rate include the degree of hydrolysis, the polymer molecular weight, crystallinity, polymer concentration, ionic strength, and the like.

**[0039]** In alternative embodiments, a degradable polymer may form rigid particulates that may be used in place of water-soluble rigid particulates. Degradation may take place by chemical, physical, or enzymatic (biological)

means, for example. Degradable polymers that may form rigid particulates suitable for use in these alternative embodiments include, for example, polysaccharides (e.g., dextran, cellulose, guar, and derivatives thereof), chitin, proteins, aliphatic polyesters [e.g., poly(hydroxy alkanoates)], polyglycolic acid and other poly(glycolides), polylactic acid and other poly(lactides), polyacrylamide and other polyacrylates, polymethacrylamide and other polymethacrylates, polyvinyl alcohol, poly( $\beta$ -hydroxy alkanoates) [e.g., poly( $\beta$ -hydroxy butyrate) and poly( $\beta$ -hydroxybutyrates-co- $\beta$ -hydroxyvalerate)], poly(hydroxybutyrates), poly( $\omega$ -hydroxy alkanoates) [e.g., poly( $\beta$ -propiolactone) and poly( $\epsilon$ -caprolactone)], poly(alkylene dicarboxylates) [e.g., poly(ethylene succinate) and poly(butylene succinate)], poly(hydroxy ester ethers), poly(anhydrides) [e.g., poly(adipic anhydride), poly(suberic anhydride), poly(sebacic anhydride), poly(dodecanedioic anhydride), poly(maleic anhydride) and poly(benzoic anhydride)], polycarbonates (e.g., trimethylenecarbonate), poly(orthoesters), poly(amino acids), poly(ethylene oxides), poly(etheresters), polyester amides, polyamides, poly(dioxepan-2-one), and polyphosphazenes. Combinations of these polymers and others may also be used in various embodiments. In various embodiments, homopolymers or copolymers of these various polymers may be used. Copolymers may include random, block, graft, and/or star copolymers in various embodiments.

**[0040]** The degradation rate of a degradable polymer may depend at least in part on its backbone structure. The degradability of a degradable polymer may be due to a chemical change, for example, that destroys the polymer structure or that changes the solubility of the polymer such that it becomes more soluble than the parent polymer. For example, the presence of hydrolysable and/or oxidizable linkages in the backbone may make a polymer degradable in one or more of the foregoing manners. The rates at which polymers degrade may be dependent on factors such as, for example, the repeat unit, composition, sequence, length, molecular geometry, molecular weight, morphology (e.g., crystallinity, particle size, and the like), hydrophilicity/hydrophobicity, and surface area. In addition, exposure to conditions such as for example, temperature, moisture, oxygen, microorganisms, enzymes, pH, and the like may alter the degradation rate. Knowing how the degradation rate is influenced by the polymer structure, one of ordinary skill in the art will be able to choose an appropriate degradable polymer

for a given application. It is to be noted that the foregoing factors may also influence the degradation rate of the gelled degradable polymers used in the present embodiments.

**[0041]** In still other alternative embodiments, a dehydrated compound may comprise the rigid particulates. A dehydrated compound, particularly a dehydrated borate, may degrade over time as the dehydrated compound rehydrates and becomes soluble. Illustrative dehydrated borates may include, for example, anhydrous sodium tetraborate (anhydrous borax) and anhydrous boric acid. These anhydrous borates and others are only slightly soluble in water. However, upon exposure to subterranean temperatures, they may slowly rehydrate over time and become considerably more soluble. As a result of the increased solubility, anhydrous borate particulates may degrade by becoming soluble. The time required for anhydrous borates to become soluble may range from between about 8 hours and about 72 hours, depending upon the temperature of the subterranean zone in which they are placed.

**[0042]** In embodiments in a non-native particulate size distribution of rigid particulates is used, the mean particulate size may range between about 1 micron and about 5 mm. In some embodiments, the mean particulate size of the rigid particulates may range between about 10 microns and about 1 mm. In some embodiments, the mean particulate size of the rigid particulates may range between about 50 microns and about 750 microns. In some embodiments, the mean particulate size of the rigid particulates may range between about 100 microns and about 500 microns. In some embodiments, the particulate size distribution of the rigid particulates may fall within about 5% of the mean particulate size. In some embodiments, the particulate size distribution of the rigid particulates may fall within about 10% of the mean particulate size. In some embodiments, the particulate size distribution of the rigid particulates may fall within about 15% of the mean particulate size. In some embodiments, the particulate size distribution of the rigid particulates may fall within about 20% of the mean particulate size. In some embodiments, the particulate size distribution of the rigid particulates may fall within about 25% of the mean particulate size. In some embodiments, the particulate size distribution of the rigid particulates may fall within about 30% of the mean particulate size.



**[0043]** In embodiments in which two or more portions of rigid particulates are combined to produce a "custom" particulate size distribution, the particulates may again range between about 1 micron and about 5 mm in size. In some embodiments, a mean size of a first portion of rigid particulates may be about 50 microns in size or less, and a second portion of rigid particulates may be about 50 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 50 microns in size or less, and a second portion of rigid particulates may be about 100 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 50 microns in size or less, and a second portion of rigid particulates may be about 150 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 50 microns in size or less, and a second portion of rigid particulates may be about 200 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 100 microns in size or less, and a second portion of rigid particulates may be about 100 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 100 microns in size or less, and a second portion of rigid particulates may be about 150 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 100 microns in size or less, and a second portion of rigid particulates may be about 200 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 100 microns in size or less, and a second portion of rigid particulates may be about 250 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 150 microns in size or less, and a second portion of rigid particulates may be about 150 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 150 microns in size or less, and a second portion of rigid particulates may be about 200 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 150 microns in size or less, and a second portion of rigid particulates may be about 250 microns in size or greater. In some embodiments, a mean size of a first portion of rigid particulates may be about 150 microns in size or less, and a second portion of rigid particulates may be about 300 microns in size or greater.

**[0044]** In some embodiments, the first portion of rigid particulates may have a smaller mean particulate size than does the second portion of rigid particulates. In some embodiments, the first portion of rigid particulates may have no particular lower limit in particulate size, while the second portion of rigid  
5 particulates may have a distinct upper and lower particulate size. In some embodiments, the first portion of rigid particulates may be about 50 microns in size or less. In some embodiments, the first portion of rigid particulates may be about 75 microns in size or less. In some embodiments, the first portion of rigid particulates may be about 100 microns in size or less. In some embodiments,  
10 the first portion of rigid particulates may be about 125 microns in size or less. In some embodiments, the first portion of rigid particulates may be about 150 microns in size or less. In some embodiments, the first portion of rigid particulates may be about 175 microns in size or less. In some embodiments, the first portion of rigid particulates may be about 200 microns in size or less.  
15 In some embodiments, the second portion of rigid particulates may range between about 100 microns and about 500 microns in size. In some embodiments, the second portion of rigid particulates may range between about 150 microns and about 500 microns in size. In some embodiments, the second portion of rigid particulates may range between about 200 microns and about  
20 500 microns in size. In some embodiments, the second portion of rigid particulates may range between about 250 microns and about 500 microns in size.

**[0045]** In various embodiments, the first portion of rigid particulates and the second portion of rigid particulates may be present in a ratio ranging  
25 between about 1:19 and about 19:1. In some embodiments, the first portion of rigid particulates may comprise at least about 10% of the total rigid particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 15% of the total rigid particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 20% of the total rigid  
30 particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 25% of the total rigid particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 30% of the total rigid particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 35% of the total rigid particulates.  
35 In some embodiments, the first portion of rigid particulates may comprise at

least about 40% of the total rigid particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 45% of the total rigid particulates. In some embodiments, the first portion of rigid particulates may comprise at least about 50% of the total rigid particulates.

5           **[0046]** In some embodiments, the sealing compositions described hereinabove may be used in various subterranean treatment operations. Such operations may vary without limitation. Functions performed by the sealing compositions in subterranean operations may include, for example, fluid loss control, fluid diversion, conformance control, and the like.

10           **[0047]** In some embodiments, the methods can comprise: providing a sealing composition comprising: a degradable polymer, and a water-soluble material comprising a first portion of rigid particulates and a second portion of rigid particulates, each portion of rigid particulates having a sealing time and a particulate size distribution associated therewith, the particulate size  
15           distributions of the first portion of rigid particulates and the second portion of rigid particulates differing from one another; determining an amount of the first portion of rigid particulates relative to the second portion of rigid particulates in the sealing composition needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the  
20           first portion of rigid particulates or the second portion of rigid particulates; introducing the sealing composition into a subterranean formation; and allowing the sealing composition to form a degradable fluid seal in the subterranean formation. In some embodiments, the methods may further comprise: performing a treatment operation in the subterranean formation while the  
25           degradable fluid seal is intact; and allowing the degradable fluid seal to degrade.

**[0048]** In some embodiments, the methods can comprise: providing a sealing composition comprising: particulates of a gelled degradable polymer, and a water-soluble material comprising rigid particulates having a sealing time and a particulate size distribution associated therewith, the particulate size  
30           distribution of the water-soluble material differing from that of a like unsized water-soluble material; determining a particulate size distribution of the rigid particulates needed to produce a degradable fluid seal having a desired sealing time; introducing the sealing composition into a subterranean formation; forming a degradable fluid seal in the subterranean formation from the sealing  
35           composition; performing a treatment operation in the subterranean formation

while the degradable fluid seal is intact; and allowing the degradable fluid seal to degrade.

**[0049]** In alternative embodiments of the foregoing methods, a degradable polymer or an anhydrous borate may comprise the rigid particulates instead of a water-soluble material.

**[0050]** In some embodiments, the sealing compositions may be introduced into a subterranean formation in a treatment fluid. In some embodiments, the treatment fluids may comprise an aqueous carrier fluid or an oil-based carrier fluid. Suitable aqueous carrier fluids may include, for example, fresh water, salt water, brine (saturated salt water), seawater, produced water (*i.e.*, subterranean formation water brought to the surface), surface water (*e.g.*, lake or river water), and flow back water (*i.e.*, water placed into a subterranean formation and then brought back to the surface). In some embodiments, the treatment fluid may be gelled so as to better support the transport of the particulates into the subterranean formation.

**[0051]** Depending upon the type of subterranean formation being treated and the intended type of treatment operation being conducted, other components may be optionally included in the treatment fluid. Such components may include, for example, salts, pH control additives, surfactants, foaming agents, antifoaming agents, breakers, biocides, crosslinkers, additional fluid loss control agents, stabilizers, chelating agents, scale inhibitors, gases, mutual solvents, particulates, corrosion inhibitors, oxidizing agents, reducing agents, antioxidants, relative permeability modifiers, viscosifying agents, proppant particulates, gravel particulates, scale inhibitors, emulsifying agents, de-emulsifying agents, iron control agents, clay control agents, flocculants, scavengers, lubricants, friction reducers, viscosifiers, weighting agents, hydrate inhibitors, consolidating agents, any combination thereof, and the like. A person having ordinary skill in the art, with the benefit of this disclosure, will recognize when such optional additives should be included in a treatment fluid, as well as the appropriate amounts to include.

**[0052]** The methods described herein may be used in many different types of subterranean treatment operations. Such operations may include, but are not limited to, acidizing operations, scale inhibiting operations, water blocking operations, clay stabilizer operations, biocide operations, fracturing operations, frac-packing operations, and gravel packing operations.

**[0053]** In some embodiments, a treatment fluid used to introduce the sealing compositions into a subterranean formation may have a basic pH. For example, a basic compound may be present in the treatment fluid. As one of ordinary skill in the art will recognize, inclusion of a basic compound in the treatment fluid may promote the degradation of a degradable polymer, particularly a poly(meth)acrylamide. Suitable basic compounds that may be used to accelerate the degradation rate of a poly(meth)acrylamide may include, for example, calcium carbonate, calcium bicarbonate, calcium oxide, magnesium oxide, magnesium hydroxide, and the like. In some or other embodiments, the treatment fluid may contain an oxidant, which may also accelerate the degradation rate of a poly(meth)acrylamide.

**[0054]** Likewise, in some embodiments, a treatment fluid used to introduce the sealing compositions into a subterranean formation may also contain an additive that accelerates the solubilization or degradation of the rigid particulates. Suitable additives may include acids, acid-generating compounds (e.g., esters and orthoesters), bases, base-generating compounds, enzymes, oxidants, solvents, oil, chelating agents, surfactants, azo compounds, buffers, catalysts, solubility-enhancing compounds, and the like. In other embodiments, the treatment fluids may also contain an additive that decelerates the solubilization or degradation of the rigid particulates. For example, for rigid particulates that oxidatively degrade, the treatment fluid may contain an antioxidant.

**[0055]** In some embodiments, the sealing compositions themselves may contain additional solid particulates that accelerate the degradation rate of the gelled degradable polymer and/or the solubilization or degradation of the rigid particulates. As previously described, inclusion of other solid particulates within the degradable fluid seal formed from the sealing compositions may create a localized chemical and/or physical environment that accelerate degradation or solubilization. Any of the foregoing additives may be included as additional solid particulates in the degradable fluid seals described herein.

**[0056]** Generally, the sealing compositions may be introduced into any type of subterranean formation. Further, the subterranean formation may have any permeability. However, as noted above, the sealing compositions may be particularly useful in high permeability formations. In some embodiments, the subterranean formation may have a permeability of at least about 0.5 darcy (D).

In other embodiments, the subterranean formation may have a permeability of at least about 1 D, or at least about 5 D, or at least about 10 D, or at least about 50 D, or at least about 100 D. In some embodiments, a high permeability subterranean formation may have at least some pore throats therein that have a nominal opening size of at least about 20  $\mu\text{m}$ .

**[0057]** In some embodiments, the degradable fluid seal formed in the subterranean formation may dissolve in a fluid present therein. Dissolution of the fluid seal may take place during or after degradation of the degradable fluid seal takes place. For example, partial dissolution of the degradable fluid seal may take place up through the time when the fluid seal fails. After fluid flow resumes in the formation, the failed seal may persist for some period of time but become soluble thereafter. In some embodiments, the degradable polymer of the fluid seal may become soluble, thereby leading to failure of the fluid seal, followed by solubilization of the rigid particulates thereafter. In other embodiments, the rigid particulates may be at least partially solubilized or degraded, thereby leading to failure of the fluid seal, followed by degradation and solubilization of the gelled degradable polymer and solubilization of the remaining rigid particulates thereafter. In some embodiments, the foregoing degradation and dissolution processes may take place concurrently.

**[0058]** In some embodiments, a sealing time of the degradable fluid seal may be altered by changing the amount of the rigid particulates having at least two different particulate size ranges relative to one another. That is, the degradation rate of the degradable fluid seal may be altered by changing the size distribution of the rigid particulates, which may be performed by mixing two or more differentially sized rigid particulates with one another. Given the benefit of the present disclosure, one having ordinary skill in the art will be able to determine a suitable combination of sized rigid particulates to produce a desired sealing time for a degradable fluid seal within a subterranean formation.

**[0059]** In some embodiments, the methods may comprise: providing a plurality of gelled degradable polymer particulates; providing a first portion of a water-soluble material and a second portion of a water-soluble material, each portion comprising rigid particulates and each portion having a sealing time and a particulate size distribution associated therewith, the particulate size distributions differing from one another; mixing the first portion of the water-soluble material and the second portion of the water-soluble material with the

plurality of gelled degradable polymer particulates, thereby forming a sealing composition; determining an amount of the first portion of the water-soluble material relative to the second portion of the water-soluble material in the sealing composition needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the first portion of the water-soluble material or the second portion of the water-soluble material; and introducing the sealing composition into a subterranean formation to form a degradable fluid seal therein. In some embodiments, the methods may further comprise: choosing the particulate size distributions of the first portion of the water-soluble material and the second portion of the water-soluble material needed to produce a degradable fluid seal having a desired sealing time.

**[0060]** 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

**[0061] EXAMPLE 1: Degradation rates of degradable fluid seals containing chopped crosslinked polyacrylamide particulates and polyvinyl alcohol particulates.** A combination of chopped crosslinked polyacrylamide particulates and polyvinyl alcohol particulates was used to form a degradable fluid seal on a 90 micron Aloxite disc (2.5" diameter). The fluid breakthrough time of the degradable fluid seal was evaluated in a high pressure, high temperature flow cell. Testing was conducted at a differential pressure of 500 psi and a temperature of 200°F. In each case, a degradable fluid seal (filter cake) was generated over 36 minutes at room temperature under a 500 psi differential pressure by flowing a treatment fluid containing the particulates through the Aloxite disc. Thereafter, fluid loss was recorded with a graduated cylinder until the filter cake was blown through.

**[0062]** The polyacrylamide was made degradable by incorporating a cleavable linkage in the polymer backbone in the form of a degradable crosslinking agent. The degradable polyacrylamide was prepared by polymerizing acrylamide with a polyethylene oxide/diacrylate oligomer having a molecular weight of 258. The polymerization reaction was conducted at ambient temperature using potassium persulfate as an initiator in the presence of

N,N,N'-tetramethylethylenediamine. The resulting polymer gel was then chopped in 40 ppt PAC-R™ filtration control agent (carboxymethyl cellulose, commercially available from Halliburton Energy Services) by using a Silverson blender operating at 6000 RPM for 1 min. The average size of the chopped  
5 particulates was about 100 microns. BARRACARB 150® bridging agent (CaCO<sub>3</sub>, commercially available from Halliburton Energy Services) was added in the chopped gels to increase the degradation rate.

**[0063]** The polyvinyl alcohol particulates were CELVOL™ 125, a highly hydrolyzed polyvinyl alcohol (99.3%) available from Celanese Corp. Two  
10 different particulate size ranges were used, as obtained from grinding and sieve-based size separation: 1) <125 microns and 2) 125 microns – 355 microns. Various compositional ratios of these sized polyvinyl alcohol particulates were used as set forth below.

**[0064]** A first treatment fluid was prepared at the following  
15 composition: 10% degradable polyacrylamide gel particulates in 400 mL of 40 ppt PAC-R™ filtration control additive, also containing 0.05 wt. % BARRACARB 150® and 1.75 wt. % CELVOL™ 125 additive. In this case, 14.3 wt. % of the CELVOL™ 125 additive had a particle size <125 microns and 85.7 wt. % had a particle size between 125 microns and 355 microns. FIGURE 1 shows an  
20 illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 14.3 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 85.7 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns. As shown in FIGURE 1, after the initial formation  
25 period at room temperature, the degradable fluid seal remained intact for more than 5 hours at 200°F under a 500 psi differential pressure.

**[0065]** A second treatment fluid was prepared at the following composition: 10% degradable polyacrylamide gel particulates in 400 mL of 40 ppt PAC-R™ filtration control additive also containing 0.05 wt. % BARRACARB  
30 150® and 1.75 wt. % CELVOL™ 125 additive. In this case, 18.6 wt. % of the CELVOL™ 125 additive had a particle size <125 microns and 81.4 wt. % had a particle size between 125 microns and 355 microns. FIGURE 2 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 18.6 wt.  
35 % of the polyvinyl alcohol particulates had a particle size <125 microns and 81.4



wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns. As shown in FIGURE 2, after the initial formation period at room temperature, the degradable fluid seal remained intact for about 140 minutes at 200°F under a 500 psi differential pressure. After fluid breakthrough occurred, the remaining degradable fluid seal was removed from the flow cell and was placed in a glass jar with 250 mL of 40 ppt PAC-R™ filtration control additive, which was subsequently heated to 200°F. Within 15 hours, the remaining degradable fluid seal had been completely removed as the remaining polyacrylamide gel particulates were degraded and the polyvinyl alcohol particulates were solubilized.

**[0066]** A third treatment fluid was prepared at the following composition: 10% polyacrylamide gel particulates in 400 mL of 40 ppt PAC-R™ filtration control additive, also containing 0.05 wt. % BARRACARB 150® and 1.75 wt. % CELVOL™ 125 additive. In this case, 21.4 wt. % of the CELVOL™ 125 additive had a particle size <125 microns and 78.6 wt. % had a particle size between 125 microns and 355 microns. FIGURE 3 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 21.4 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 78.6 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns. As shown in FIGURE 3, after the initial formation period at room temperature, the degradable fluid seal remained intact for about 80 minutes at 200°F under a 500 psi differential pressure.

**[0067]** A fourth treatment fluid was prepared at the following composition: 10% polyacrylamide gel particulates in 400 mL of 40 ppt PAC-R™ filtration control additive, also containing 0.05 wt. % BARRACARB 150® and 1.75 wt. % CELVOL™ 125 additive. In this case, 28.6 wt. % of the CELVOL™ 125 additive had a particle size <125 microns and 71.4 wt. % had a particle size between 125 microns and 355 microns. FIGURE 4 shows an illustrative fluid breakthrough plot of a treatment fluid containing crosslinked polyacrylamide particulates and polyvinyl alcohol particulates in which 28.6 wt. % of the polyvinyl alcohol particulates had a particle size <125 microns and 71.4 wt. % of the polyvinyl alcohol particulates had a particle size between 125 microns and 355 microns. As shown in FIGURE 4, after the initial formation period at room

temperature, the degradable fluid seal remained intact for about 30 minutes at 200°F under a 500 psi differential pressure.

**[0068]** The foregoing series of tests illustrate that a combination of chopped degradable polyacrylamide gel particulates and polyvinyl alcohol particulates can be used to produce a degradable fluid seal. The rate at which the fluid seal fails and permits fluid flow to resume can be altered by combining sized polyvinyl alcohol particulates in various ratios with one another.

**[0069]** Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be

incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

## CLAIMS

The invention claimed is:

1. A method comprising:
  - providing a sealing composition comprising:
    - a degradable polymer, and
    - a water-soluble material comprising a first portion of rigid particulates and a second portion of rigid particulates, each portion of rigid particulates having a sealing time and a particulate size distribution associated therewith, the particulate size distributions of the first portion of rigid particulates and the second portion of rigid particulates differing from one another;
  - determining an amount of the first portion of rigid particulates relative to the second portion of rigid particulates in the sealing composition needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the first portion of rigid particulates or the second portion of rigid particulates;
  - introducing the sealing composition into a subterranean formation; and
  - allowing the sealing composition to form a degradable fluid seal in the subterranean formation.
2. The method of claim 1 wherein the water-soluble material comprises a water-soluble polymer.
3. The method of any of the preceding claims wherein the water-soluble polymer comprises at least one polymer selected from the group consisting of polyvinyl alcohol, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, carboxyethyl cellulose, acetyl cellulose, hydroxyethyl cellulose, shellac, chitosan, chitin, dextran, guar, xanthan, starch, a scleroglucan, a diutan, poly(vinyl pyrrolidone), polyacrylamide, polyacrylic acid, poly(diallyldimethylammonium chloride), poly(ethylene glycol), poly(ethylene oxide), polylysine, polymethacrylamide, polymethacrylic acid, poly(vinylamine), any derivative thereof, any copolymer thereof, and any combination thereof.
4. The method of any of the preceding claims wherein the degradable polymer comprises particulates of a gelled degradable polymer.

5. The method of any of the preceding claims wherein the degradable polymer comprises at least one crosslinked polymer selected from the group consisting of a crosslinked polyacrylamide, a crosslinked polymethacrylamide, any hydrolyzed or partially hydrolyzed variant thereof, any derivative thereof, any copolymer thereof, and any combination thereof.
6. The method of any of the preceding claims wherein the degradable polymer comprises at least one crosslinked polymer selected from the group consisting of a crosslinked polyacrylamide, a crosslinked polymethacrylamide, any hydrolyzed or partially hydrolyzed variant thereof, any derivative thereof, any copolymer thereof, and any combination thereof.
7. The method of any of the preceding claims wherein the sealing composition is introduced into the subterranean formation in a treatment fluid having a basic pH.
8. The method of any of the preceding claims wherein at least a portion of the subterranean formation has a permeability of at least about 0.5 D.
9. The method of any of the preceding claims further comprising:
  - performing a treatment operation in the subterranean formation while the degradable fluid seal is intact; and
  - allowing the degradable fluid seal to degrade.
10. A method comprising:
  - providing a sealing composition comprising:
    - particulates of a gelled degradable polymer, and
    - a water-soluble material comprising rigid particulates having a sealing time and a particulate size distribution associated therewith, the particulate size distribution of the water-soluble material differing from that of a like unsized water-soluble material;
  - determining a particulate size distribution of the rigid particulates needed to produce a degradable fluid seal having a desired sealing time;
  - introducing the sealing composition into a subterranean formation;
  - forming a degradable fluid seal in the subterranean formation from the sealing composition;
  - performing a treatment operation in the subterranean formation while the

degradable fluid seal is intact; and  
allowing the degradable fluid seal to degrade.

11. The method of claim 10 wherein, during or after degrading, the degradable fluid seal dissolves in a fluid present in the subterranean formation.

12. The method of claim 10 or 11, wherein the water-soluble material comprises a first portion of rigid particulates and a second portion of rigid particulates, each portion having a sealing time and a particulate size distribution associated therewith, the particulate size distributions of the first portion of rigid particulates and the second portion of rigid particulates differing from one another.

13. The method of claim 12, wherein a sealing time of the degradable fluid seal can be altered by changing an amount of the first portion of rigid particulates relative to the second portion of rigid particulates.

14. The method of claim 10, 11, 12, or 13, wherein the water-soluble material comprises a water-soluble polymer.

15. The method of claim 14, wherein the water-soluble polymer comprises at least one polymer selected from the group consisting of polyvinyl alcohol, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, carboxyethyl cellulose, acetyl cellulose, hydroxyethyl cellulose, shellac, chitosan, chitin, dextran, guar, xanthan, starch, a scleroglucan, a diutan, poly(vinyl pyrrolidone), polyacrylamide, polyacrylic acid, poly(diallyldimethylammonium chloride), poly(ethylene glycol), poly(ethylene oxide), polylysine, polymethacrylamide, polymethacrylic acid, poly(vinylamine), any derivative thereof, any copolymer thereof, and any combination thereof.

16. The method of claim 10, 11, 12, 13, 14, or 15, wherein herein the gelled degradable polymer comprises at least one crosslinked polymer selected from the group consisting of a crosslinked polyacrylamide, a crosslinked polymethacrylamide, any hydrolyzed or partially hydrolyzed variant thereof, any derivative thereof, any copolymer thereof, and any combination thereof.

17. The method of claim 16, wherein the sealing composition is introduced into the subterranean formation in a treatment fluid having a basic pH.
18. The method of claim 10, 11, 12, 13, 14, 15, 16, or 17, wherein at least a portion of the subterranean formation has a permeability of at least about 0.5 D.
19. A method comprising:  
providing a plurality of gelled degradable polymer particulates;  
providing a first portion of a water-soluble material and a second portion of a water-soluble material, each portion comprising rigid particulates and each portion having a sealing time and a particulate size distribution associated therewith, the particulate size distributions differing from one another;  
mixing the first portion of the water-soluble material and the second portion of the water-soluble material with the plurality of gelled degradable polymer particulates, thereby forming a sealing composition;  
determining an amount of the first portion of the water-soluble material relative to the second portion of the water-soluble material in the sealing composition needed to produce a degradable fluid seal having a desired sealing time that is different than that of the sealing time of either the first portion of the water-soluble material or the second portion of the water-soluble material;  
and  
introducing the sealing composition into a subterranean formation to form a degradable fluid seal therein.
20. The method of claim 19, further comprising:  
choosing the particulate size distributions of the first portion of the water-soluble material and the second portion of the water-soluble material needed to produce a degradable fluid seal having a desired sealing time.
21. The method of claim 19 or 20, wherein the water-soluble material comprises a water-soluble polymer.
22. The method of claim 21, wherein the water-soluble polymer comprises at least one polymer selected from the group consisting of polyvinyl alcohol, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, carboxyethyl cellulose, acetyl cellulose, hydroxyethyl cellulose, shellac, chitosan, chitin, dextran, guar, xanthan, starch, a scleroglucan, a diutan, poly(vinyl pyrrolidone),

polyacrylamide, polyacrylic acid, poly(diallyldimethylammonium chloride), poly(ethylene glycol), poly(ethylene oxide), polylysine, polymethacrylamide, polymethacrylic acid, poly(vinylamine), any derivative thereof, any copolymer thereof, and any combination thereof.

23. The method of claim 19, 20, 21, or 22, wherein the gelled degradable polymer comprises at least one crosslinked polymer selected from the group consisting of a crosslinked polyacrylamide, a crosslinked polymethacrylamide, any hydrolyzed or partially hydrolyzed variant thereof, any derivative thereof, any copolymer thereof, and any combination thereof.



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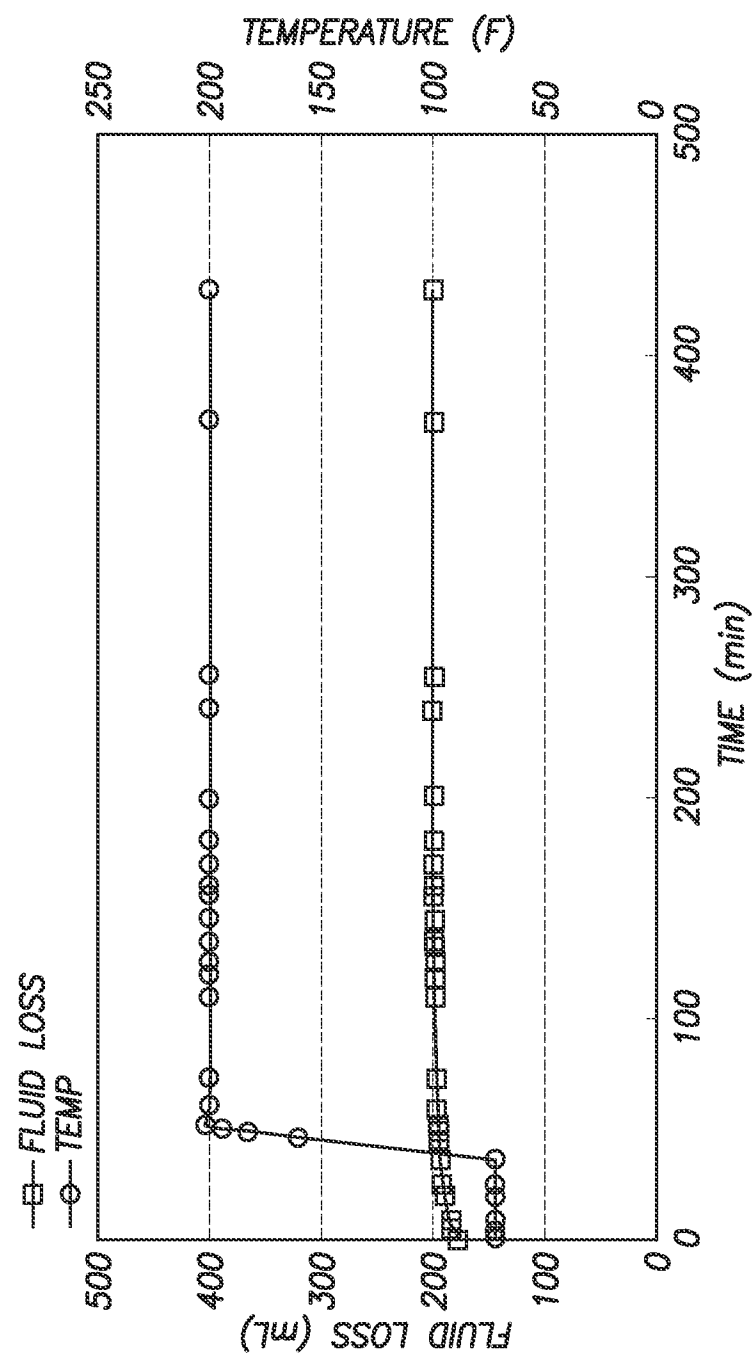


FIG.1

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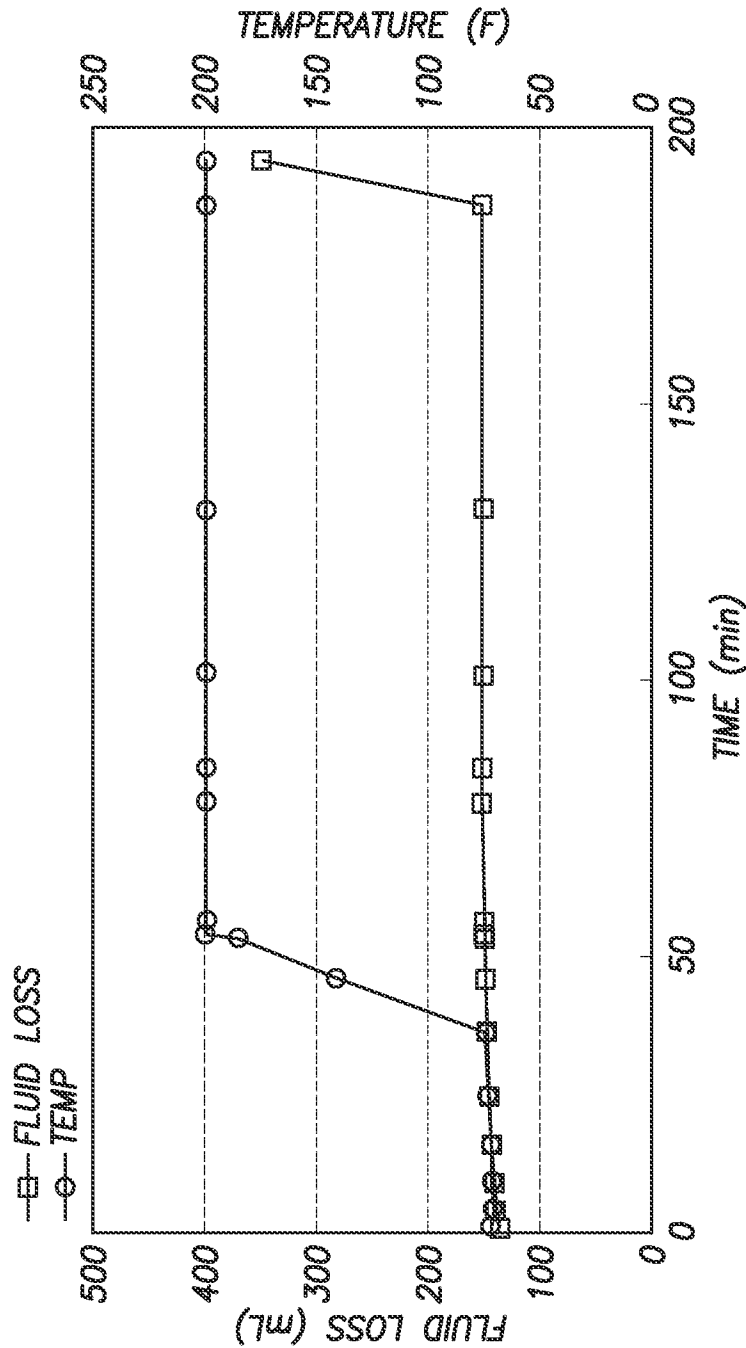


FIG.2

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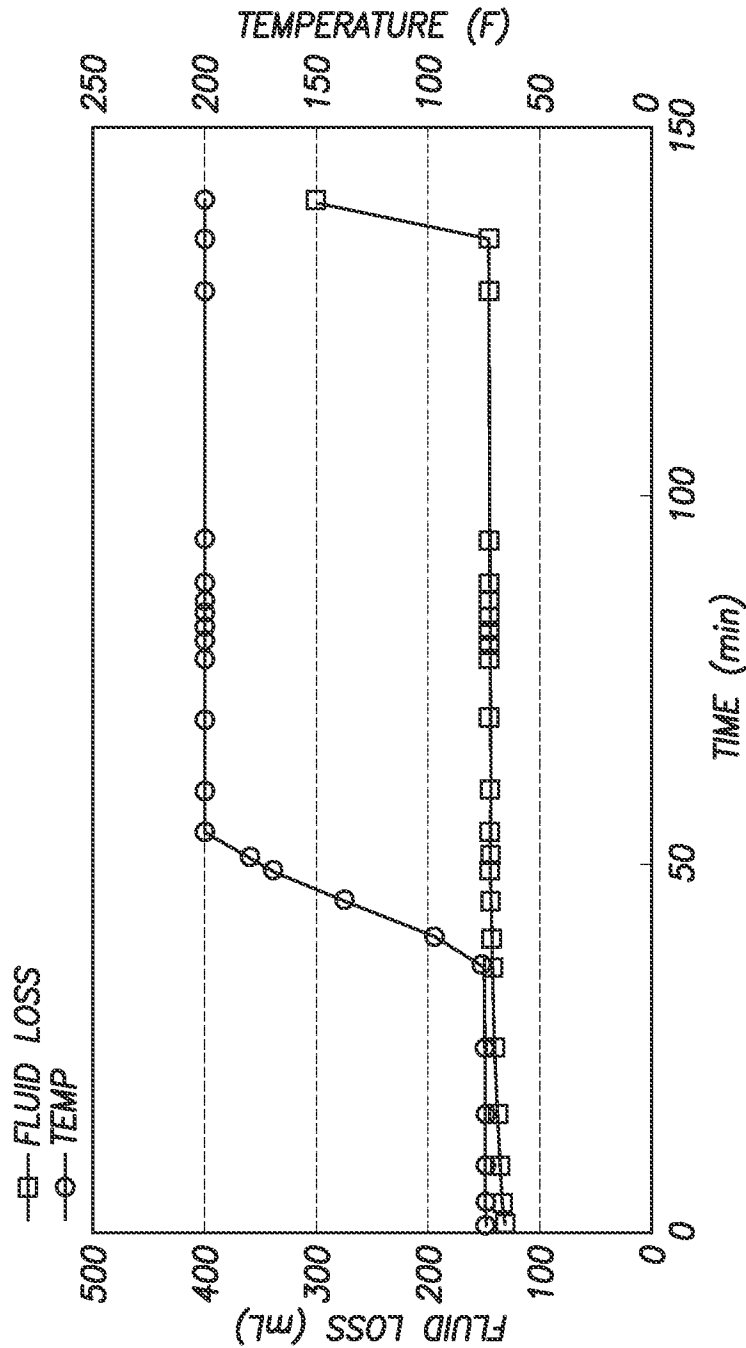


FIG.3

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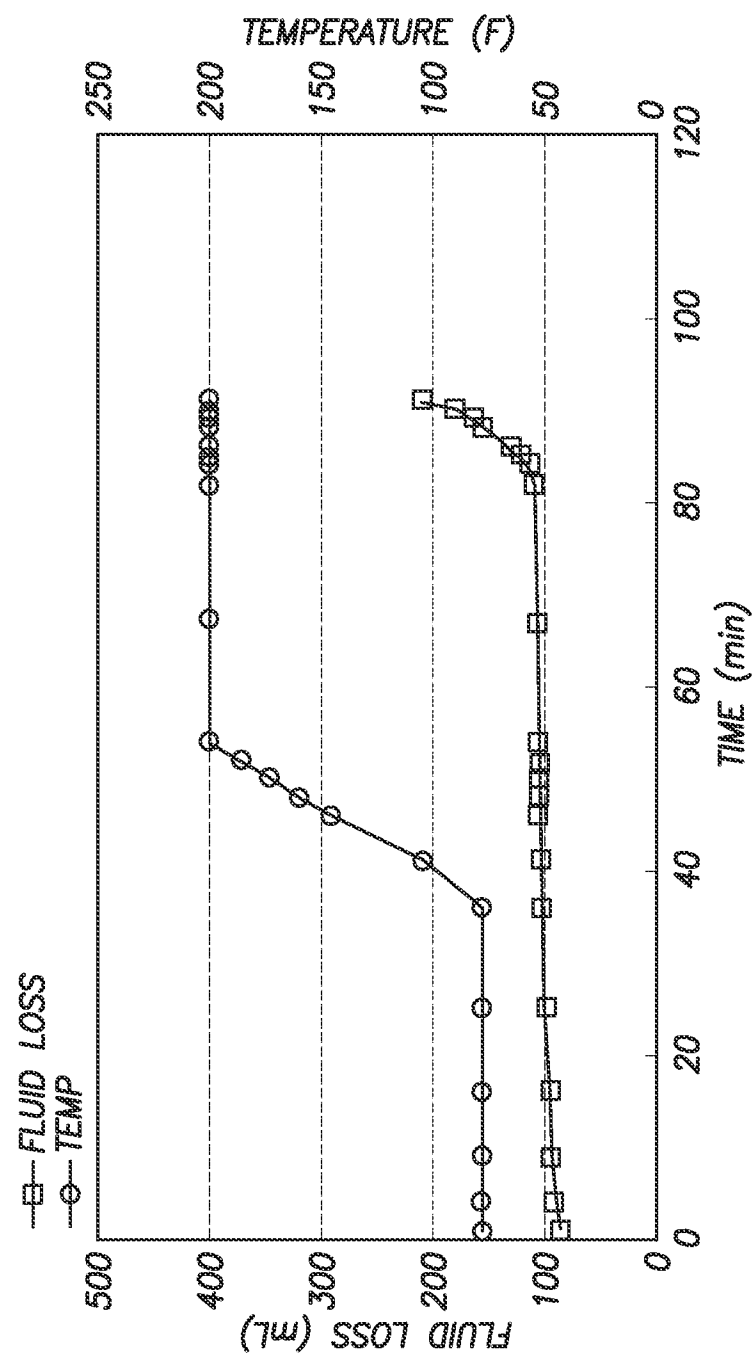


FIG. 4

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/027863

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/512 C09K8/035  
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

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Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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"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

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"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

10 April 2013

Date of mailing of the international search report

17/04/2013

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Straub, Thomas

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2013/027863

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
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Information on patent family members

International application No

PCT/US2013/027863

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