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Sinclair et al.(10) **Pub. No.: US 2006/0175059 A1**(43) **Pub. Date: Aug. 10, 2006**(54) **SOLUBLE DEVERTING AGENTS****Publication Classification**(76) Inventors: **A. Richard Sinclair**, Houston, TX
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HOWREY LLP**C/O IP DOCKETING DEPARTMENT****2941 FAIRVIEW PARK DRIVE, SUITE 200****FALLS CHURCH, VA 22042-7195 (US)**(21) Appl. No.: **11/336,344**(22) Filed: **Jan. 20, 2006****Related U.S. Application Data**

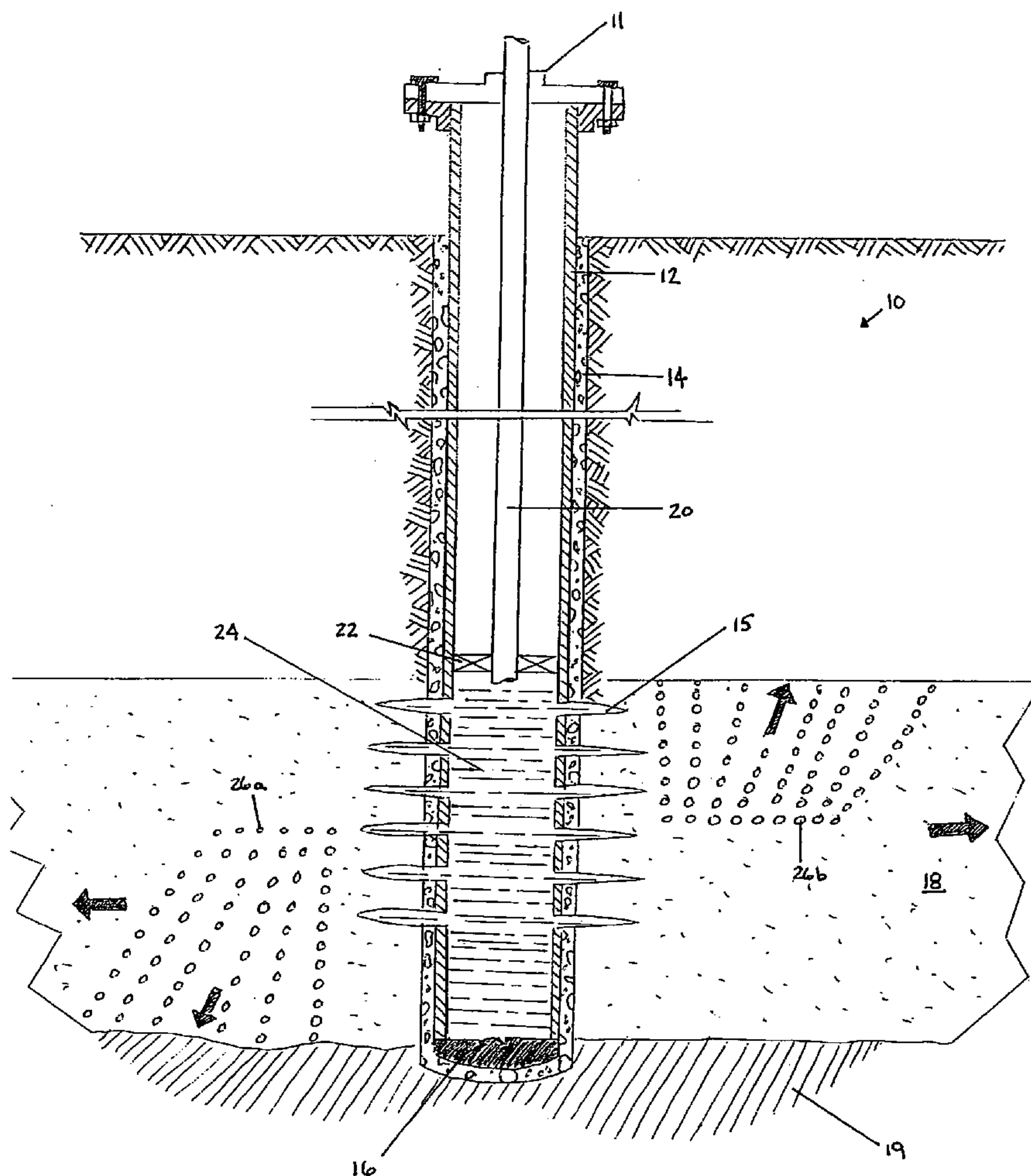
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(57)

ABSTRACT

Methods and compositions for stimulating single and multiple intervals in subterranean wells by diverting well treatment fluids into a particular direction or into multiple intervals using water soluble coated diverting agents are described. The water soluble coating of the diverting material is preferably a collagen, poly(alkylene) oxide, poly(lactic acid), polyvinylacetate, polyvinylalcohol, polyvinylacetate/polyvinylalcohol polymer or a mixture thereof applied as a coating on any number of proppants. The method allows for the diverting of the flow of fluids in a downhole formation during a well treatment, such as during a fracturing process. Following completion of a treatment such as a hydraulic stimulation, the soluble diverting agent can be dissolved and removed by the water component of the well production.



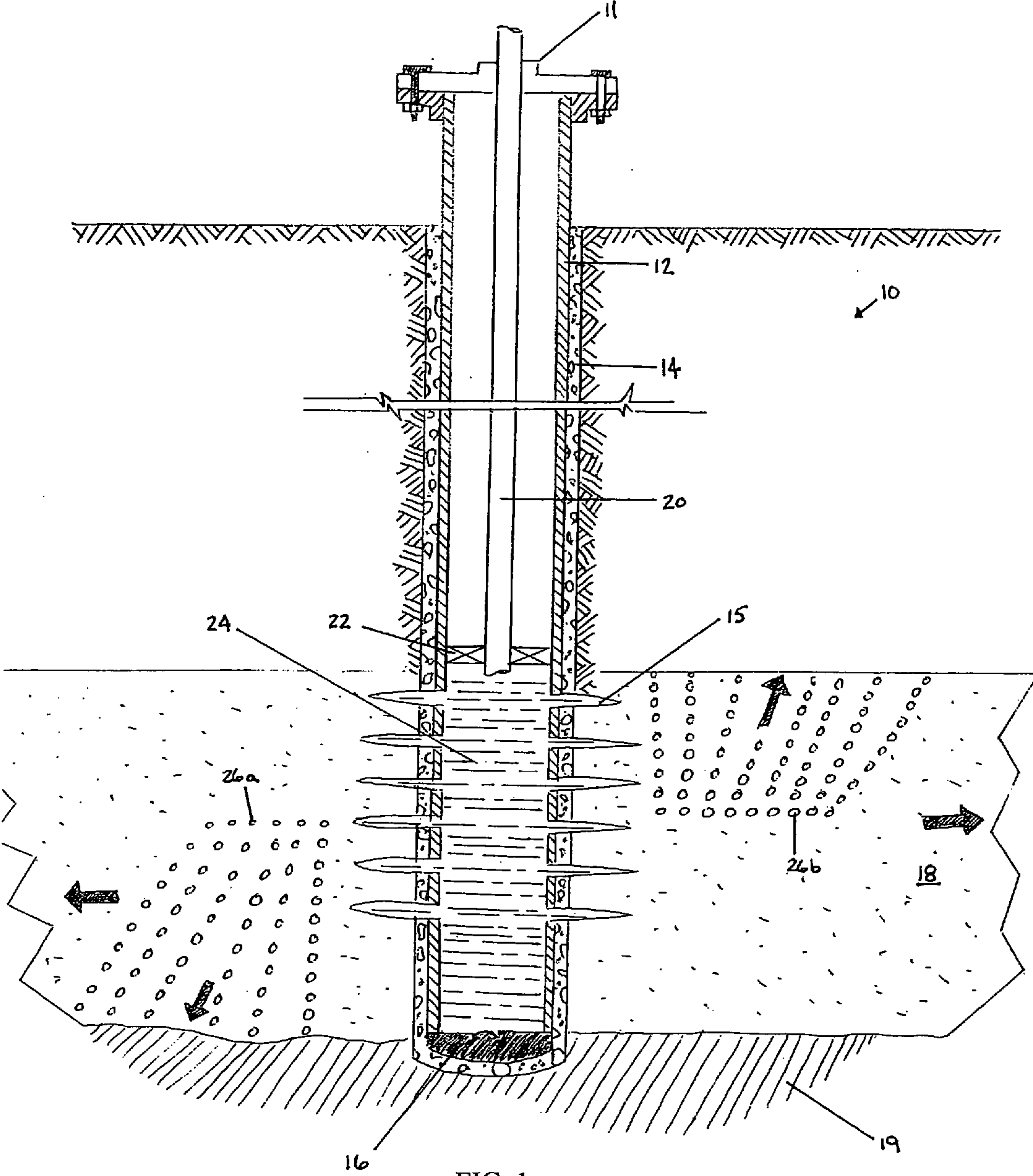


FIG. 1

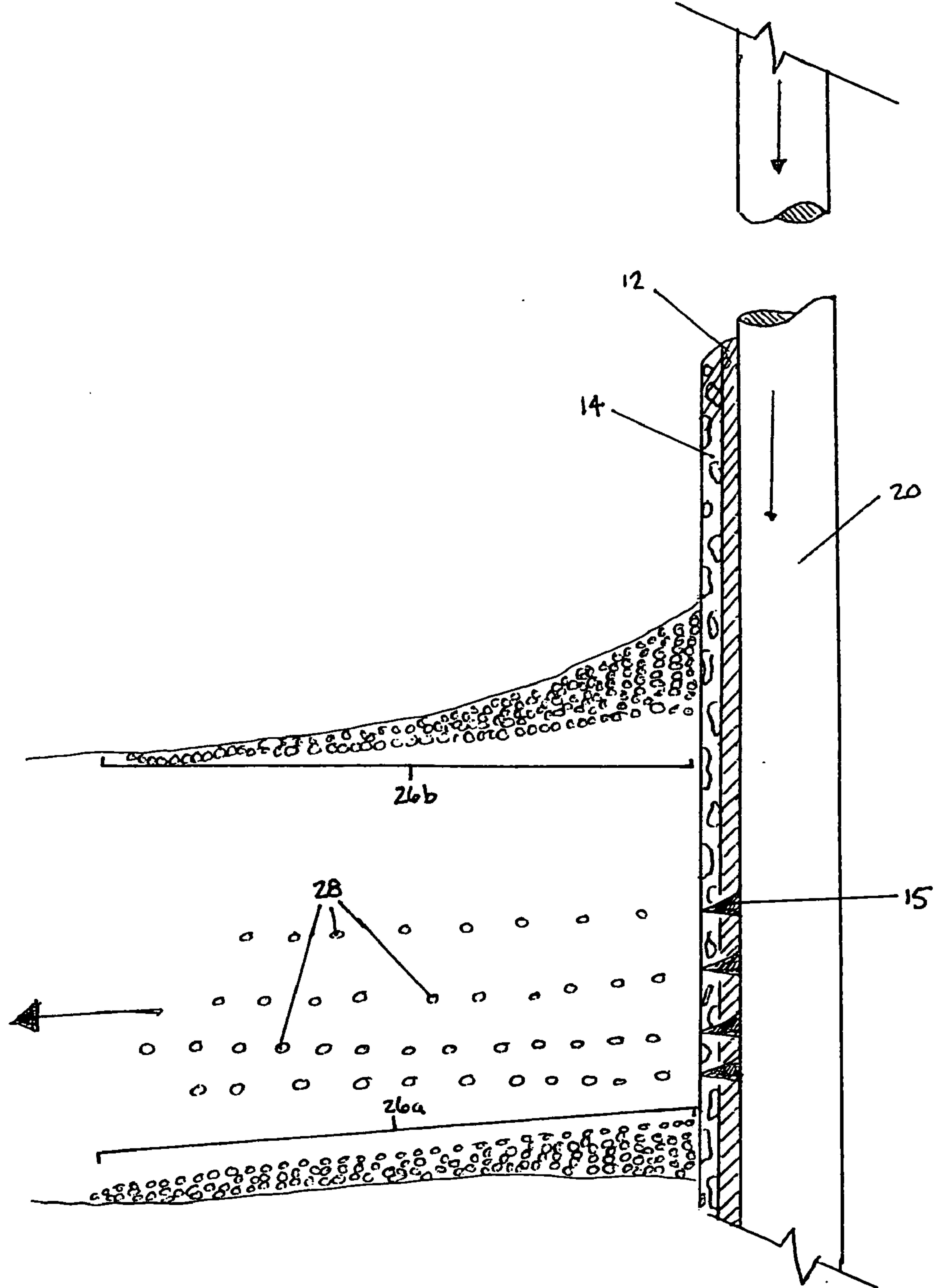


FIG. 2

SOLUBLE DEVERTING AGENTS

[0001] The present application claims priority benefit to U.S. provisional application Ser. No. 60/646,231 filed Jan. 21, 2005, the entire contents of which are incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention provides methods and compositions for treating subterranean wells and, more specifically, provides methods and compositions for stimulating multiple intervals in subterranean wells. In particular, this invention provides methods and compositions for diverting well treatment fluids into multiple intervals by introducing propping materials coated with a water soluble polymer e.g. collagen, polyvinyl acetate/polyvinyl alcohol, polyalkyl oxides, poly(lactic acid), periodic chart elements of group I or II (alkali metal or alkaline earth metal) silicate polymer, or combinations thereof with materials that are slowly water soluble for use in redirecting the flow of stimulation fluids from a tubing string into the subterranean environment.

DESCRIPTION OF RELATED ART

[0003] Well treatments, such as acid and fracture treatments of subterranean formations are routinely used to improve or stimulate the recovery of hydrocarbons. In many cases, a subterranean formation may include two or more intervals having varying permeability and/or injectivity. Some intervals may possess relatively low injectivity, or ability to accept injected fluids, due to relatively low permeability, high in-situ stress, and/or formation damage. Such intervals may be completed through preparations in a cased wellbore and/or may be completed open hole. In some cases, such formation intervals may be present in a highly deviated or horizontal section of a wellbore, for example, a lateral open hole section. In any case, when treating multiple intervals having variable injectivity it is often the case that most, if not all, of the introduced well treatment fluid will be displaced into one, or only a few, of the intervals having the highest injectivity. Even if there is only one interval to be treated, the tendency for the growth of the fracture can be either up or down. This depends on the in situ formation stress and the permeability variation in the formation layer. Below the created fracture can be a water zone. If the created fracture breaks into this zone, the well can be ruined due to excess water and a cut off of the petroleum components of the productive interval. Above the created fracture zone a gas cap may exist which would cause harm to the production of the well because of gas bypassing the liquid petroleum components of the well.

[0004] In an effort to more evenly distribute displaced well treatment fluids into each of the multiple intervals being treated, methods and materials for diverting treatment fluids into intervals of lower permeability and/or injectivity have been developed. However, conventional diversion techniques may be costly and/or may achieve only limited success. In this regard, mechanical diversion techniques are typically complicated and costly. Furthermore, mechanical diversion methods are typically limited to cased hole environments and depend upon adequate cement and tool isolation for achieving diversion.

[0005] The efficient and simultaneous treatment of multiple sets of perforations over an extended vertical section

has thus been a problem in well stimulation for numerous years. Numerous treatment diversion methods, such as oil-soluble calcium soap, sulfuric acid, and Dowell's "Fixafac" (a mixture of lime, kerosene, a graded calcium chloride soap, and a gelling agent, and Dowell's FLAX-2™ as described by Harrison in his comprehensive review *Journal of Petroleum Technology*, pp. 593-598 (1972), have been used to treat multiple zones with a wide variety of effectiveness. A great variety of chemical based diverting agents have been used in attempts to plug formation openings and divert treating fluids to other zones of the formation. For example, wax beads have been used as diverting agents. However, the wax beads have limited melting points, from about 138° F. to about 192° F., making them useless if the formation temperature exceeds their melting point.

[0006] Naphthalene (moth balls) and sodium chloride particles have also been described to be useful as effective diverting agents. Naphthalene particles are readily soluble in oil, but melt at about 180° F., thereby limiting their use to applications in lower-temperature formations. Sodium chloride, having a melting point of about 1,470° F., while useful at high temperatures, requires that the well be cleaned with water or dilute acid after the formation has been treated in order to fully remove the sodium chloride particles. Furthermore, sodium chloride cannot be used with hydrofluoric acid to treat subterranean wells due to the formation of insoluble precipitates which can problematically block the wellbore.

[0007] Alternatively, diversion agents such as polymers, suspended solid materials and/or foam have been employed when simultaneously treating multiple intervals of variable injectivity. Such diversion agents are typically pumped into a subterranean formation prior to a well treatment fluid in order to seal off intervals of higher permeability and divert the well treatment fluid to intervals of lower permeability. However, the diverting action of such diversion agents is often difficult to predict and monitor, and may not be successful in diverting treatment fluid into all desired intervals. These problems may be further aggravated in open hole completions, especially in highly deviated completions having large areas of a formation open to the wellbore. The presence of natural fractures may also make diversion more difficult.

[0008] Several attempts to address the issues of areas of differing permeability within a wellbore have been addressed over the years. U.S. Pat. No. 2,803,306 to Hower offers a process for increasing the permeability of an underground formation having several zones of varying permeability. The steps described include introducing into a well bore a treatment fluid containing hydrochloric acid which has oil-soluble particles dispersed therein, the material being selected from gilsonite, naphthalene, para-dichlorobenzene, anthracene, and β -naphthol. Upon treatment, the particles provide a partial blockage of the more permeable zones of the subterranean formation, allowing the treatment fluid to enter the less-permeable zones.

[0009] U.S. Pat. No. 3,797,575 assigned to Halliburton discloses diverting-forming additives comprised of relatively water insoluble solid material dissolved in a solvent such as methanol or isopropanol. When the additive is combined with an aqueous treatment fluid, the solid material, dissolved in the additive, is precipitated in the aqueous

treating fluid into a finally divided form, which then act as a diverting agent. U.S. Pat. No. 3,724,549, also assigned to Halliburton, describes a diverting agent material for diverting aqueous treatment fluids into progressively less permeable subterranean formations. The material is composed of a carrier liquid and graded particles of cyclic or linear hydrocarbon resins having between about 20 and about 1,400 carbon atoms, and a melting point of about 200° F. This material is described as being largely water and acid insoluble, but soluble in oil, such that the resin can be removed by the produced oil after the completion of the oil treatment operation.

[0010] The use of radiation-induced polymers as either temporary or permanent diverting agents has been described by Knight, et al. in U.S. Pat. No. 3,872,923. According to the specification, temporary or permanent reductions in permeability can be obtained by injecting an aqueous solution containing a water-soluble polymer obtained by radiation-induced polymerization of acrylamide and/or methacrylamide and acrylic acid, methacrylic acid, and/or alkali metal salts of such acids. The resultant polymeric diverting agent has properties, such as temperature and pH stability, so as to effect a reduction of permeability of the porous medium. Permeability within the formation can be restored by subsequent treatment with a chemical to break down the polymer, such as hydrazine hypochlorite solution or strong mineral acids.

[0011] U.S. Pat. Nos. 3,954,629 and 4,005,753 to Scheffel, et al., offer polymeric diverting agents, and methods of treating subterranean formations with such polymeric diverting agents, respectively. The polymeric composition is described to comprise solid particles of a homogenous mixture of polyethylene, ethylene-vinyl acetate copolymer, a polyamide, and a softening agent such as long chain aliphatic diamides. These polymeric diverting agents are reported to be suitable for use in subterranean formations where formation temperatures are 350° F. or greater.

[0012] Methods of temporarily plugging a subterranean formation using a diverting material comprising an aqueous carrier liquid and a diverting agent comprising a solid azo component and a methylenic component are described by Dill, et al. in U.S. Pat. No. 4,527,628. The diverting agent is preferably Hansa Yellow G (Fanchon Yellow YH-5707 pigment) or Fast Yellow 4RLF dye, both of which have an azo component and a methylenic component and are further characterized as having a melting point of at least 332.6° F., a degree of solubility in water at a temperature of water from about 200 to about 425° F., and a degree of solubility in kerosene at a temperature of from about 200° F. to about 425° F.

[0013] In U.S. Pat. No. 6,367,548, Purvis, et al. describes methods and compositions for stimulating multiple intervals in subterranean wells by diverting well treatment fluids into multiple intervals. According to the specification, this is accomplished by alternately displacing diverting agent from the annulus of the wellbore into a subterranean formation and displacing treatment fluid from a tubing string into the subterranean formation.

[0014] Other methods for diverting a fracture treatment include the limited-entry technique described by LaGrone, et al., SPE 530, pp. 695-702 (1963), and the Technique of Multi-Fracture Fracturing Using a Diverting Agent

(TMFUD) suggested by Dingxiang, et al., SPE 30816, pp. 80-86 (1988), the latter of which has shown an average oil production improvement of 15.0 t/d for each well, and a cumulative production improvement of 340.3×10^4 tons. A viscoelastic surfactant-based diverting agent for use in acid stimulations has also been described (Alleman, D., et al., SPE 80222 (2003)), which is a VES gel (polyQuat) characterized by a distinctive vesicle structure stable at high pH and a thermal stability of about 250° F. This gel-type diversion agent is typically pumped into a subterranean formation prior to a well stimulation fluid in order to seal off intervals of high permeability and divert the well treatment fluid to intervals of low permeability.

[0015] In light of all these advances and new techniques, the diverting action of diverting agents is often difficult to predict and monitor, and may not be successful in diverting treatment fluid into all the desired intervals, thereby failing to allow maximum benefit from the fracture procedure. These problems can be further aggravated in open hole completions, especially in highly-deviated completions having large areas of a formation open to the wellbore. The presence of natural fractures within the subterranean formation can also serve to make diversion more challenging. Thus, there exists a need for new compositions and methods for diverting well treatment fluids into multiple intervals of varying permeability within a subterranean formation.

SUMMARY OF THE INVENTION

[0016] The present invention provides a method of using particles having a soluble outer coating as diverting agents in subterranean formations. The soluble outer coating will dissolve after a desired period of time at downhole temperatures and pressures in the presence of standard downhole fracturing fluids and breaker compositions. Examples of the soluble outer coating include collagen, poly(alkylene) oxides, poly(lactic acid), polyvinylacetate, polyvinyl alcohol, polyvinylacetate/polyvinylalcohol, polylactone, polyacrylate, latex, polyester, group I or II silicate polymer or mixtures thereof.

[0017] The present invention provides water soluble polymer coated proppants as diverting agents and methods of using such diverting agents for treating a subterranean formation. The diverting agent together with a carrier liquid is introduced into a subterranean formation. The liquid carrier flows into fractures and/or intervals within the subterranean formation. The fractures or intervals present varying degrees of permeability. In accordance with the methods of the present invention, the liquid carrier with diverting agent will flow to the most permeable interval first. The temperature of the formation will cause the water soluble polymer coating of the diverting agent to soften and swell, thereby plugging the fracture.

[0018] In one embodiment, a diverting agent suitable for diverting well treatment fluids into a single or a multiple interval is described, wherein the diverting agent is comprised of a particulate substrate and a water-soluble outer layer. Such water soluble outer layer polymer is exemplified, without limitation, by collagen, poly(alkylene) oxides, poly(lactic acid) polyvinylacetate, polyvinylalcohols, polyvinylacetate/polyvinylalcohol, polymeric lactones, water-soluble acrylics, latex, polyester, group I or II silicate polymer, and admixtures thereof.

[0019] In a further embodiment, a diverting agent suitable for diverting well treatment fluids into a single or a multiple interval is described, wherein the diverting agent is comprised of a particulate substrate an intermediate water insoluble layer and a water soluble polymer outer layer. The water soluble outer layer polymer is exemplified, without limitation, by collagen, poly(alkylene) oxides, poly(lactic acid), polyvinylacetate, polyvinylalcohols, polyvinylacetate/polyvinylalcohol, polymeric lactones, water-soluble acrylics, latex, polyester, group I or II silicate polymer and admixtures thereof. The water insoluble intermediate layer is exemplified by phenol-aldehyde novolac polymers and phenol-aldehyde resole polymers.

[0020] In yet another embodiment, a diverting agent suitable for diverting well treatment fluids into a single or a multiple interval within a wellbore is described, wherein the diverting agent is substantially a water-soluble polymer particle such as a collagen bead or granular particles of poly(alkylene) oxide, poly(lactic acid), polyvinylacetate, polyvinylalcohol, polyvinylacetate/polyvinylalcohol, polymeric lactones, water-soluble acrylics, latex, polyester, group I or II silicate polymer, or mixtures thereof.

[0021] In a further embodiment, a method of stimulating individual intervals of a subterranean formation is disclosed, the method including the steps of introducing a diverting agent having a water-soluble component on its outer layer into an inner pipe of a wellbore in combination with a low viscosity fluid or a fracturing fluid; displacing the diverting agent and fracturing fluid into the subterranean formation, allowing the diverting agent to progressively plug portions of the formation being treated; and repeating the process as necessary, adding the diverting agent to the carrier fluid in slugs during the fracturing operation.

DESCRIPTION OF THE FIGURES

[0022] The following figures form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these figures in combination with the detailed description of specific embodiments presented herein.

[0023] **FIG. 1** shows an elevational cross-sectional view of a downhole portion of a subterranean formation having a vertical casing and a single treatment interval, wherein variously coated diverting agents are being injected into the hydrocarbon-bearing formation in accordance with an aspect of the present disclosure.

[0024] **FIG. 2** illustrates the elevational cross-sectional view of the subterranean formation of **FIG. 1**, wherein proppants are being injected into a hydrocarbon-bearing formation having diverting agents of the present invention injected.

[0025] **FIG. 3** shows a well with a vertical casing and multiple treatment intervals **58**, **60** and **62** and variously coated diverting agents being injected, in accordance with an aspect of the present disclosure.

DEFINITIONS

[0026] The following definitions are provided in order to aid those skilled in the art in understanding the detailed description of the present invention.

[0027] The term “carrier liquid” as used herein refers to oil or water based liquids that are capable of moving particles (e.g., proppants) that are in suspension. Low viscosity carrier fluid have less carrying capacity and the particles can be affected by gravity so that they either rise if they are less dense than the liquid or sink if they are more dense than the liquid. High viscosity liquids can carry particles with less settling or rising since the viscosity overcomes gravity effects.

[0028] The term “crosslinker” or “cross-linking agent”, as used herein, refers to those compounds used to covalently modify proteins, such as collagen, and includes both homobifunctional crosslinkers that contain two identical reactive groups, and heterobifunctional crosslinkers which contain two different reactive groups.

[0029] The term “diverting agent”, as used herein, means and refers generally to an agent that functions to prevent, either temporarily or permanently, the flow of a liquid into a particular location, usually located in a subterranean formation, wherein the agent serves to seal the location and thereby cause the liquid to “divert” to a different location.

[0030] The term “proppant”, as used herein, refers to those sized particles that are used in well work-overs and treatments, such as hydraulic fracturing operations, to hold fractures open following the treatment. Such sized particles are often mixed with fracturing fluid(s) to hold fractures open after a hydraulic fracturing treatment or similar down-hole well treatment. In addition to naturally occurring sand grains and nut hulls, the term “proppant” includes man-made or specially engineered proppants, such as resin-coated sand or high-strength ceramic materials like sintered bauxite. Resin coated proppants are typified by those that are coated with phenol-aldehyde novolac polymers or phenol-aldehyde resole polymers. Typically, but not necessarily, proppant materials are carefully sorted for size and sphericity to provide an efficient conduit for production of fluid from the reservoir to the wellbore.

[0031] In embodiments described and disclosed herein, the use of the term “introducing” includes pumping, injecting, pouring, releasing, displacing, spotting, circulating, or otherwise placing a fluid or material within a well, wellbore, or subterranean formation using any suitable manner known in the art. Similarly, as used herein, the terms “combining”, “contacting”, and “applying” include any known suitable methods for admixing, exposing, or otherwise causing two or more materials, compounds, or components to come together in a manner sufficient to cause at least partial reaction or other interaction to occur between the materials, compounds, or components.

[0032] The term “water soluble” as used herein refers to resins, polymers, or coatings which are stable (do not dissolve) under ambient, surface conditions, but which become soluble after a given time (usually over several hours or several days) when placed in a subterranean environment.

[0033] The term “treatment”, as used herein, refers to any of numerous operations on or within the downhole well, wellbore, or reservoir, including but not limited to a work-over type of treatment, a stimulation type of treatment, such as a hydraulic fracturing treatment or an acid treatment, isolation treatments, control of reservoir fluid treatments, or

other remedial types of treatments performed to improve the overall well operation and productivity.

[0034] The term “stimulation”, as used herein, refers to productivity improvement or restoration operations on a well as a result of a hydraulic fracturing, acid fracturing, matrix acidizing, sand treatment, or other type of treatment intended to increase and/or maximize the well’s production rate or its longevity, often by creating highly conductive reservoir flow paths.

DETAILED DESCRIPTION OF THE INVENTION

[0035] In embodiments of the disclosed diverting agent, single and multiple intervals of a subterranean formation can be treated or stimulated in stages by successively introducing the diverting agent comprising a particulate substrate and a slowly water-soluble outer coating comprising collagen or a combination of collagen and a slowly water-soluble, non-collagenous material.

[0036] The invention provides particle compositions comprising soluble material coatings comprising collagen, as well as processes for preparing such compositions. These compositions are useful in subterranean formations for diverting well treatment fluids in a single interval to increase the fracture length or in multiple intervals of a subterranean formation having varying permeability and/or injectivity during a hydraulic fracturing operation. In using the diverting agents of the present invention in fracturing processes, the proppant (or particulate substrate) coated with a slowly water-soluble coating such as a collagen alone or in combination with a non-collagenic water-soluble, plastic coating material acts to divert the fracture, as the coatings on the proppants act as the defining boundaries of the initial fracture. Following the fracturing treatment, the coating can be removed due to the slow-dissolution characteristics of the coating, leaving standard propping agents with high permeability to flow into the fracture and act as proppants.

[0037] While compositions and methods are described in terms of “comprising” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps.

A. Substrate

[0038] Particulate material, also referred to herein as substrate material, suitable for use with the present invention includes a variety of particulate materials known to be suitable or potentially suitable propping agents which can be employed in downhole operations. In accordance with the present invention, the particulate material (or substrate material) which can be used include any propping agent suitable for hydraulic fracturing known in the art. Examples of such particulate materials include, but are not limited to, natural materials, silica proppants, ceramic proppants, metallic proppants, synthetic organic proppants, mixtures thereof, and the like.

[0039] Natural products suitable for use as proppants include, but are not limited to, nut shells such as walnut, brazil nut, and macadamia nut, as well as fruit pits such as peach pits, apricot pits, olive pits, and any resin impregnated or resin coated version of these. Typical resin coatings or impregnations include bisphenols, bisphenol homopolymers, blends of bisphenol homopolymers with phenol-alde-

hyde polymer, bisphenol-aldehyde resins and/or polymers, phenol-aldehyde polymers and homopolymers, modified and unmodified resoles, phenolic materials including arylphenols, alkylphenols, alkoxyphenols, and aryloxyphenols, resorcinol resins, epoxy resins, novolak polymer resins, novolak bisphenol-aldehyde polymers, and waxes, as well as the precured or curable versions of such resin coatings.

[0040] Silica proppants suitable for use with the present invention include, but are not limited to, glass spheres and glass microspheres, glass beads, silica quartz sand, and sands of all types such as white or brown. Typical silica sands suitable for use include Northern White Sands (Fairmount Minerals, Chardon, Ohio), Ottawa, Jordan, Brady, Hickory, Arizona, St. Peter, Wonowoc, and Chalfort, as well as any resin coated version of these sands. In the case of silica fibers being used, the fibers can be straight, curved, crimped, or spiral shaped, and can be of any grade, such as E-grade, S-grade, and AR-grade. Examples of suitable resin-coated silica proppants for use with the present invention include deformable proppants such as FLEXSAND LSTTM and FLEXSAND MSTTM (available from BJ Services, Inc., Houston, Tex.) and Tempered HS[®], Tempered LC[®], Tempered DC[®], and Tempered TF[®] tempered proppants, all available from Santrol, Fresno, Tex.

[0041] Ceramic proppants suitable for use with the methods of the present invention include, but are not limited to, ceramic beads; spent fluid-cracking catalysts (FCC) such as those described in U.S. Pat. No. 6,372,378, which is incorporated herein in its entirety; ultra lightweight porous ceramics; economy lightweight ceramics such as “ECONOPROPTM” (Carbo Ceramics, Inc., Irving, Tex.); lightweight ceramics such as “CARBOLITETM”; intermediate strength ceramics such as “CARBOPROPTM” (available from Carbo Ceramics, Inc., Irving, Tex.); high strength ceramics such as “CARBOHSPTM” and “Sintered Bauxite” (Carbo Ceramics, Inc., Irving, Tex.), and HYPERPROP G2TM, DYNAPROP G2TM, or OPTIPROP G2TM encapsulated, curable ceramic proppants (available from Santrol, Fresno, Tex.) as well as any resin coated or resin impregnated versions of these, such as described above.

[0042] Metallic proppants suitable for use with the embodiments of the present invention include, but are not limited to, aluminum shot, aluminum pellets, aluminum needles, aluminum wire, iron shot, steel shot, and the like, as well as any resin coated versions of these metallic proppants.

[0043] Synthetic proppants are also suitable for use with the present invention. Examples of suitable synthetic proppants include, but are not limited to, plastic particles or beads, nylon beads, nylon pellets, SDVB (styrene divinyl benzene) beads, carbon fibers such as PANEXTM carbon fibers from Zoltek Corporation (Van Nuys, Calif.), and resin agglomerate particles similar to “FLEXSAND MSTTM” (BJ Services Company, Houston, Tex.), as well as resin coated versions thereof.

[0044] Additionally, soluble materials suitable for use as proppants are also envisioned to be useful with the methods of the present invention. For example, soluble proppants which are placed in the channels of the created perforations include, but are not limited to, marble or limestone chips or any other suitable carbonate particulates. Additionally, wax,

plastic, or resin particles, either coated or uncoated, which are either soluble through contact with a treatment chemical or can melt and flowback from the fracture are suitable for use as proppants with the present invention.

[0045] Suitable with the present invention, propping agents are typically used in concentrations from about 1 to about 18 pounds per gallon (about 120 g/L to about 2,160 g/L) of fracturing fluid composition, but higher or lower concentrations may also be used as required.

[0046] Similarly, the particulate substrate suitable for use with the present invention has a particle size in the range of USA Standard Testing screen numbers from about 4 to about 200 (i.e., screen openings of about 0.18 inch to about 0.003 inch). More particularly, particulate substrate sizes suitable for use with the present invention include size ranges from about 4 mesh (4750 microns) to about 200 mesh (75 microns). Also suitable for use with the present invention are particulate materials or proppants having size-designations of 6/12, 8/16, 12/18, 12/20, 16/20, 16/30, 20/40, 30/50, 40/70 and 70/140, although any desired size distribution can be used, such as 10/40, 14/20, 14/30, 14/40, 18/40, and the like, as well as any combination thereof (e.g., a mixture of 10/40 and 14/40). The preferred mesh size, in accordance with the present invention, is 20/40 mesh.

B. Soluble Coating

[0047] The soluble coatings used in accordance with the present invention can be any number of known soluble agents that are slowly soluble in downhole, subterranean formations over a period of time. Soluble polymer materials used in accordance with the present invention should be soluble (that is, capable of dissolving in) in brines, water, oil, organic solvents, acid or acidic media, and/or in fluids having a pH in the range from about 1 to about 14, as well as mixtures thereof under the conditions found in downhole, subterranean formation.

[0048] Preferably, the soluble coating is a structural protein such as collagen or atelocollagen, a vegetable protein such as found in wheat, maize, oat or almonds, or a collagen originating from a marine environment. The latter type of collagen can be extracted from fish, algae, plankton, microplankton, and the like. More preferably, the soluble coating is collagen, including Type I collagen, Type II collagen, Type III collagen, Type IV, or Type V collagen, as well as combinations thereof. Most preferably, in accordance with the present invention, the soluble coating is a Type I collagen or an atelocollagen.

[0049] Type I collagens or atelocollagens suitable for use as soluble coatings in accordance with the present invention are those collagens containing at least one hydroxyproline residue. Such Type I collagens or atelocollagens include collagens found in tendons, skin, bone, scar tissue, and the like, such as tropocollagens, as well as products derived from the controlled, enzymatic or chemical reduction of collagen proteins. Such collagens preferably have a molecular weight from about 10,000 Daltons to about 500,000 Daltons, and more preferably from about 100,000 Daltons to about 300,000 Daltons. Suitable molecular weights of about 100,000 daltons, 125,000 daltons, 150,000 daltons, 175,000 daltons, 200,000 daltons, 225,000 daltons, 250,000 daltons, 275,000 daltons, 300,000 daltons, as well as molecular weights between any two of these values, e.g., collagens

having a molecular weight from about 225,000 to about 275,000 daltons. For example, a preferred Type I collagen suitable for use with the present invention is tropocollagen with a molecular weight of about 250,000 as supplied by Milligans and Higgins, Inc. (Johnstown, N.Y.).

[0050] Collagens suitable for use within the present invention have Bloom strengths from about 100 psi to about 900 psi, and more preferably from about 300 psi to about 700 psi. Most preferably, collagens suitable for use with the present invention have Bloom strengths from about 400 psi to about 600 psi. Suitable Bloom strengths, in accordance with the present invention, are about 400 psi, about 410 psi, about 420 psi, about 430 psi, about 440 psi, about 450 psi, about 460 psi, about 470 psi, about 480 psi, about 490 psi, about 500 psi, about 510 psi, about 520 psi, about 530 psi, about 540 psi, about 550 psi, about 560 psi, about 570 psi, about 580 psi, about 590 psi, and about 600 psi, as well as Bloom strengths between any two of these values, e.g., from about 400 psi to about 520 psi, such as 512 psi.

[0051] Bloom strength, as used herein, refers to the measured value of the strength and/or rigidity of a gelatinous substance, such as collagen, formed by a standard solution of definite concentration that has been retained at a constant temperature for a specified period of time, in accordance with standardized bloom testing procedures, such as BS757:1975, GMIA Testing Standard B5757, International Standard ISO9665 for testing adhesive animal glues, or similar standards as described in "*Official Methods of Analysis of AOAC INTERNATIONAL (OAM)*", 17th Edition, Volume II; AOAC International Publications (2003). Bloom strength values are typically given in "pounds per square inch" (psi) or grams, reflecting the force required to depress a chosen area of the surface of the sample a distance of 4 mm. In a typical procedure, a gel product, such as collagen or gelatin, is formed to a specified consistency (e.g., 6 and 2/3% solution) and kept at a constant temperature in a constant temperature bath at 10 C. for 18 hours. A device called a Texture Analyzer (e.g., the TA.XT2i Texture Analyzer, Scarsdale, N.Y.) then measures the weight in grams (or the pressure, in psi) required to depress a standard AOAC® [Association of Official Analytical Chemists] gelometer plunger having a sharp, lower edge 4 mm into the gel; alternatively, a BS plunger which has a bottom edge rounded to a radius of 0.4 mm can be used as the plunger. For example, if this procedure requires 200 grams to depress the plunger, then the gelatin has a Bloom strength of 200.

[0052] Type I collagens suitable for use within the present invention have a sieve distribution/size designation of 6/12, 8/16, 12/1.8, 12/20, 16/20, 16/30, 20/40, 30/50, 40/70 and 70/140, as well as sieve distributions between any two of these designations, although any desired size distribution can be used, such as 8/40, 10/40, 14/20, 14/30, 14/40, 18/40, and the like, as well as any combination thereof (e.g., a mixture of 10/40 and 14/40). The preferred mesh size, in accordance with the present invention, is 8/40 mesh.

[0053] Collagens, as used herein as soluble coatings, can be either cross-linked, uncross-linked, or a combination of both, and the type and degree of cross-linking will depend upon the specific application of the collagen-based soluble coating. There are four fundamental strategies for fixing collagenous materials and materials constructed of processed collagen fibers or purified collagen. These include

exogenous chemical cross-linking using agents that covalently couple neighboring collagen fibrils using targeted reactive moieties in the collagen fibrillar system and the cross-linking molecules themselves; physiochemical cross-linking techniques such as photo-oxidation, microwave irradiation, dehydration and dehydrothermal treatment, that covalently join collagen fibrils via the naturally occurring reactive amino acid side chains; chemical catalysis of intramolecular cross-links between amino acid side chains on the collagen fibrils; and polymerizing compounds mixed with collagenous assemblies and forming polymeric non-covalent or covalent interactions that do not chemically react with collagen fibrils [Koob, T. J., "Collagen Fixation", in *Encyclopedia of Biomaterials and Biomedical Engineering*, Wnek, G. E., Bowlin, G. L., Eds., 2004]. In accordance with the present invention, the collagen used as a soluble coating is preferably cross-linked using chemical cross-linking techniques. These include, but are not limited to, aldehyde-based cross-linking techniques, polyepoxy compound-based cross-linking techniques, the use of isocyanates, carbodiimide cross-linking, and acyl azide based crosslinking. More preferably, the collagen is cross-linked using aldehyde-based cross-linking techniques, such as by using glutaraldehyde or formaldehyde.

[0054] Aldehyde-based cross-linking techniques includes those techniques using a reagent containing two reactive aldehyde groups to form covalent cross-links between neighboring collagen proteins, especially the ϵ -amino groups of lysine residues in collagen [Khor, E., *Biomaterials*, Vol. 18: pp. 95-105 (1997)]. Aldehydes suitable for use with the present invention include but are not limited to glutaraldehyde, formaldehyde, propionaldehyde, and butyraldehyde.

[0055] Polyepoxy based cross-linking techniques and agents include the use of compounds, such as short, branched polymers, terminating in reactive epoxy functionalities. Polyepoxy compounds suitable for use as cross-linking agents in the present invention include but are not limited to glycerol ethers, glycol, and glycerol polyglycidyl ethers.

[0056] Isocyanates are also suitable for use as cross-linking agents in the present invention. Generally, the isocyanates ($R-NCO$) react with primary amines to form a urea bond ($R-H-CO-NH-R$); difunctional isocyanates therefore have the ability to cross-link collagen via its lysine side chains. Isocyanates suitable for use as cross-linking agents in the present invention are preferably diisocyanates, including biphenyl diisocyanate, dimethoxy-4,4'-biphenyl diisocyanate, dimethyl-4,4'-biphenyl diisocyanate, 1,3-bis(isocyanatomethyl)benzene, phenyl diisocyanate, toluene diisocyanate, tolylene diisocyanate, diisocyanato hexane, diisocyanato octane, diisocyanato butane, isophorone diisocyanate, xylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, phenylene diisocyanate, and poly(hexamethylene diisocyanate). Preferably, the isocyanate used as a cross-linking agent of the collagen molecules of the present invention is hexamethylene diisocyanate.

[0057] Carbodiimide cross-linking agents and techniques can also be used within the scope of the present invention. These agents react with the carboxyl groups of aspartic and glutamic acid side chains within the collagen to form

isoacylurea derivatives/iso-peptide bonds [Khor, E., *ibid.*]. Carbodiimides suitable for use as cross-linking agents with the collagen of the present invention include but are not limited to N,N'-dicyclohexylcarbodiimide (DCC); N,N'-diisopropylcarbodiimide (DIC); N,N'-di-tert-butylcarbodiimide; 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC; EDAC); water-soluble EDC (WSC); 1-tert-butyl-3-ethylcarbodiimide; 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide; bis(trimethylsilyl)carbodiimide; 1,3-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl)carbodiimide (BDDC, as described in U.S. Pat. No. 5,602,264); N-cyclohexyl-N'-(2-morpholinoethyl) carbodiimide; N,N'-diethylcarbodiimide (DEC); 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate [e.g., Sheehan, J. C., et al., *J. Org. Chem.*, Vol. 21: pp. 439-441 (1956)]; oligomeric alkyl cyclohexylcarbodiimides, such as those described by Zhang, et al. [*J. Org. Chem.*, Vol. 69: pp. 8340-8344 (2004)]; polymer bound DCC; and polymer bound EDC, such as cross-linked N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide on JANDAJEL™. Additionally, N-hydroxysuccinimide (NHS), 1-hydroxy-7-azabenzotriazole (HOAt), or similar reagents can be utilized in conjunction with the carbodiimide to minimize internal rearrangement of the activated isoacylurea derivative and provide more efficient cross-linking.

[0058] As with carbodiimide treatment, acyl azide crosslinking agents produce covalent bonds between the carboxylic acid side chains of aspartic acid and glutamic acids and the ϵ -amino groups of the lysines of collagen [Petit, H., et al., *J. Biomed. Mater. Res.*, Vol. 24: pp. 179-187 (1990)]. Following esterification of the carboxyl groups in which a methyl group is added to the acid, the biomaterial is treated with hydrazine to form the corresponding hydrazide; sodium nitride is then added to react with the hydrazide and form the acyl azide. Any number of hydrazines known in the art can be used in this method, including maleimidopropionic acid hydrazide (MPH).

[0059] Other chemical cross-linking agents suitable for use in the present invention to provide cross-linked collagen molecules which act as soluble coatings on proppant particles include but are not limited to homobifunctional cross-linkers such as BMME, BSOCOES, DSP (a thio-cleavable cross-linker), DSS, EGS, water-soluble EGS, and SATA, as well as heterobifunctional cross-linking agents including GMB, MBS, PMPI, SMCC, SPDP, and MPH (maleimidopropionic acid hydrazide), MCH, EMCH (maleimidocapronic acid hydrazide), KMHU (N-(k-Maleimidoundecanoic acid)hydrazide), and MPBH (4-(4-N-MaleimidoPhenyl)butyric acid hydrazide), all available from Interchim (Cedex, France).

[0060] Other techniques suitable for crosslinking the collagen fibers for use as soluble proppant coatings include but are not limited to dehydration, UV irradiation at 254 nm, glucose-mediated cross-linking (glycation) in conjunction with UV irradiation, and biological cross-linking. The latter technique includes using natural products such as genipin and its related iridoid compounds which are isolated from the fruits of the gardenia plant (*Gardenia jasminoides*), which are dialdehydes in aqueous solution and thereby can react with the ϵ -amino groups on lysine side chains of neighboring collagen molecules to provide a cross-link. Other biological cross-linking systems suitable for use with the present invention include catechol-quinone tanning sys-

tems, such as 3,4-dihydroxytyramine, and nordihydroguaiaretic acid (NDGA), isolated from the creosote bush, which acts as a cross-linking agent via the two catechols on NDGA [Koob, T. J., *Comp. Biochem. Physiol., Part A*, Vol. 133: pp. 1171-1192 (2002)].

[0061] The slowly water-soluble coatings on the particulate substrates, in accordance with the present disclosure, can also be non-collagenic materials such as synthetic polymers that are slowly water soluble. Such non-collagenic materials include but are not limited to: polyethylene oxides, polypropylene oxides, polycaprolactones; grafts of polyethylene/polypropylene and polycaprolactones; grafts of polyethylene/polypropylene oxides and polycaprolactones; water soluble or water reducible acrylics; water reducible phenoxy resin; latex; polyesters; soluble block copolymers; grafts of polyvinyl alcohol (PVA) and polyvinyl acetates; polyactides and derivatives of polylactic acid; polyglycolic acid (PGA); polyglycoliclactic acid (PGLA). Also useful for a water soluble coating are periodic chart elements of group I or II (alkali metal or alkaline earth metal) silicate polymers, e.g. SOLOSIL™ (Foseco International, Ltd., Great Britain), a sodium silicate polymer.

C. Method of Using

[0062] In embodiments of the disclosed method, single or multiple intervals of a subterranean formation may be treated or stimulated in stages by successively introducing diverting agent of the present invention into the formation followed by introduction of well treatment fluid into the formation. As used herein, "wellbore" includes cased and/or open hole sections of a well, it being understood that a wellbore may be vertical, horizontal, or a combination thereof. The term "pipe string" refers to any conduit suitable for placement and transportation of fluids into a wellbore including, but not limited to, tubing, work string, drill pipe, coil tubing, etc. Furthermore, it will be understood with benefit of this disclosure that the disclosed diversion agents and diversion treatment techniques are suitable for use with any type of well treatment fluid including, but not limited to, acid treatments, condensate treatments, hydraulic fracture treatments, and the like. Furthermore, it will be understood that the benefits of the disclosed methods and compositions may be realized with well treatments performed below, at, or above a fracturing pressure of a formation.

[0063] First: WELLBORE USE: In this aspect of the invention, the use of fully soluble particles in the wellbore (such as collagen or other water soluble polymer plastics or mixtures of these) to divert fluid flow from one zone to another and then dissolve is disclosed. The use of collagen (in both the uncrosslinked and crosslinked form) and soluble plastics are useful in diverting the flow of fluids in the well. These diverting materials should be in the range of 1 to 100 mesh size, preferably 4 to 50 mesh size and can be used in combination with other additives or plastic materials to enhance performance by diverting the flow of fluids from one zone to another.

[0064] These materials have been used as diverting ball sealers but recent tests have shown that the material could be used as a diverting agent to block fluid from flowing into one zone and into another of either higher pore pressure or lower permeability.

[0065] The present invention provides a method treating a cased wellbore to divert flow of fluids from one zone to

another. The method involves pumping into a wellbore a diverting fluid that is made up of an aqueous carrier liquid having dispersed therein a particulate form of a water soluble polymer and wherein the particulate polymer has a density greater than or less than the density of the carrier liquid. As the diverting fluid is pumped into the wellbore the particulate polymer settles into zones of the wellbore and thereby diverts flow of a treating fluid from one zone to another. Generally the treating fluid is diverted or blocked from flowing into a zone of higher pore pressure or lower permeability.

[0066] In the methods of this invention relating to wellbore use, the water-soluble particulate polymer is collagen, poly(alkylene) oxide, poly(lactic acid), polyvinylacetate, polyvinylalcohol, polyvinylacetate/polyvinylalcohol, polylactone, polyacrylate, latex, polyester, periodic chart elements of group I or II (alkali metal or alkaline-earth metal) silicate polymer or mixtures thereof. Typically the particulate polymer is present in the carrier liquid in an amount from about 0.001 pounds per gallon to about 10 pounds per gallon of the carrier liquid. Advantageously, the particulate polymer is comprised of varying densities greater or less than the density of the carrier fluid. Typically, the carrier liquid is water, brine, aqueous acid solutions, or gelled acid solutions.

[0067] Second: GENERATED FRACTURE USE: In this aspect of the invention, the use of coated particles of various propping agents (coated with either fully soluble or a mix of soluble and insoluble collagen or polymeric plastic materials) can be pumped into the fractured formations to prevent fractures from diverting out of the producing zone. For example, a dense sintered bauxite particle with a soluble or partially soluble coating would fall to the bottom of the fracture and divert the fracture from the lower strata or a water zone. Also, a low-density walnut shell with a soluble or partially soluble coating would tend to rise inside the fracture to divert the fracture from upward growth into a gas or water zone. The coating can be either fully or partially soluble since the proppant will remain in place in the fracture and provide conductivity in the fracture after the frac job is completed. Some of the coating on the proppant should be soluble but a mixture of both soluble and insoluble plastics or collagen is desirable to prevent movement of the propping agent in the fracture.

[0068] The use of diverting agents in fractures is that a proppant or propping agent would be coated with a soluble or partially soluble coating—using a collagen and/or polymeric plastic coating material or any mixture of these. The fracture would be diverted by using these soluble coatings on proppants as the defining boundaries of the initial fracture. After the fracturing treatment, the coating would disappear and the previously coated particles would return to normal propping agents, which have high permeability. Coatings on various density proppants could cause the fracture boundaries to be set early in the fracture process since a low viscosity fluid would allow a high density coated proppant to settle or fall inside the fracture to make a lower boundary on the fracture and divert it out from the wellbore to make a longer fracture and increase the productivity of the well. Likewise, a low density coated proppant would tend to rise to the top part of the growing fracture to form a top boundary and divert the growing fracture away from upper zones that may harm the production of the well. With the

fracture contained at top and bottom the fracture could grow outward and a longer contained fracture would improve the well potential productivity.

[0069] **FIG. 1** illustrates a well with a vertical cased wellbore section and a single interval formation that is to be treated in accordance with one embodiment of the present disclosure. The well **10** of **FIG. 1** has a casing **12** extending from the wellhead **11** for at least a portion of its length and is cemented around the outside with cement sheath **14** to hold the casing **12** in place and isolate the penetrated formation or intervals. The cement sheath **14** extends upward from the bottom of the wellbore in the annulus between the outside of the casing **12** and the inside wall of the wellbore at least to a point above the producing strata/hydrocarbon bearing formation **18**. The reasons for the inclusion of this sheath are many, but essentially the cement sheath **14** helps to ensure the integrity of the well-bore (i.e., so it does not collapse), or to isolate specific, different geologic zones (i.e., an oil-bearing zone from an (undesirable) water-producing zone). The wellbore is also optionally equipped with a casing or liner shoe **16** so as to help guide the casing string **12** past ledges or obstacles during its placement in the wellbore. For the hydrocarbons in the producing strata **18** to be produced, it is necessary to establish fluid communication between the producing strata **18** and the interior of casing **12**. This is accomplished by perforations **15** made through casing **12** and the cement sheath **14** by means known to those of ordinary skill in the art. Such means include, but are not limited to, perforation guns, shaped charge devices, and phase charge devices, such as those described in U.S. Pat. Nos. 6,755,249, 5,095,099, and 5,816,343; Horizontal Oriented Perforating Systems (HOPS), such as those manufactured by Owen Oil Tubes, Inc. (Ft. Worth, Tex.); mechanical perforating devices such as laterally movable punches (U.S. Pat. No. 2,482,913), needle punch perforators, and toothed wheel perforators such as those described in U.S. Pat. No. 4,220,201; and shearable plugs such as described in U.S. Pat. No. 4,498,543. The perforations **15** form a flow path for fluid from the formation into the casing **12**, and vice-versa.

[0070] The hydrocarbons flowing out of the producing strata **18** through the perforations **15** and into the interior of the casing **12** can be transported to the surface through a production tubing **20**. A production packer, **22**, can optionally be installed near the lower end of the production tubing **20** and above the highest perforation **15** in order to achieve a pressure seal between the production tubing **20** and the casing **12**. Optionally, and equally acceptable in accordance with the present invention, production tubings **20** need not be used, in which case the entire volume of casing **12** is used to conduct the hydrocarbons to the surface of the earth.

[0071] When diversion is needed during a well treatment operation, heavy weight proppant diverting agents **26a** and/or light weight proppant diverting agents **26b**, both of which are substantially coated with a soluble coating in accordance with the present invention (i.e., have a collagen-containing coating), are used to substantially seal the upper and lower sections of the producing strata **18**. This substantial sealing, or border formation, occurs when the temporary diverting agents **26a** and/or **26b** are introduced into the casing **12** at a predetermined time during the treatment. When the diverting agents **26a** and/or **26b** are introduced into the fluid upstream of the perforated parts of the casing **12**, they are

carried down the production tubing **20** or casing **12** by the treating fluid **24** flow. Once the treating fluid **24** arrives at the perforated interval in the casing, it flows outwardly through the perforations **15** and into the strata **18** being treated. The flow of the treating fluid **24** through the perforations **15** carries the temporary diverting agents **26a** and/or **26b** through the perforations and out into the strata **18**. At this point, the heavy weight proppant diverting agents **26a**, having a density greater than that of the treating fluid **24**, settle to the bottom of the created fracture (as indicated by the arrows), forming a temporary “lower border” between the fracture and, for example a sand, shale or clay layer **19** or other area to which it is desirable to seal off from the producing strata. Similarly, light weight proppant diverting agents **26a**, having a density less than that of treating fluid **24**, rise to the top of the created fracture (as indicated by the arrows), thereby forming another temporary “upper border” between the fracture and an undesirable layer, such as a shale or clay band of strata.

[0072] **FIG. 2** illustrates the next step of this aspect of the present invention. Once the temporary diverting agents **26a** and **26b** are seated at the top and/or bottom of the created fracture, respectively, the fluid flow rate and viscosity of the treating fluid **24**, containing regular proppant particles **28**, is increased. In this manner, the fracture can grow outward, away from the wellbore (in the direction of the arrow) and in doing so increase the overall length of the fracture, thereby aiding in increasing the stimulation and/or longevity of the well. At the completion of the well treatment, the soluble coating on the temporary diverting agents **26a** and **26b** will dissolve, allowing the remaining proppant particles to be removed with the treating fluid **24** through perforations **15**, or to remain and act as additional proppants in propping open the fractured strata.

[0073] **FIG. 3** illustrates a further embodiment of the present invention. A well **50** having a vertical cased wellbore with a casing **54** extended from the wellhead **52** for at least a portion of the length of the wellbore, and a cement sheath **56** extending upwards from the bottom of the wellbore in the annulus between the outside of the casing **54** and the inside wall of the wellbore, at least to a point above the existing strata, similar to that shown in **FIG. 1**. Exposed within the open hole section of the wellbore is a subterranean formation having multiple treatment intervals **58**, **60** and **62**. Although three separated intervals are illustrated in **FIG. 3**, it will be understood with benefit of this disclosure that anywhere from two treatment intervals up to any number of treatment intervals can be treated using the presently disclosed methods and compositions. Furthermore, it will be understood that such treatment intervals can be contiguously disposed rather than separated by relatively impermeable areas such as shale breaks. Although **FIG. 3** illustrates a fully cased wellbore, it will also be understood that disclosed treatment methods may be utilized with virtually any type of wellbore completion scenario. For example, the disclosed methods may advantageously be employed to treat well configurations including, but not limited to, vertical wellbores, fully cased wellbores, horizontal wellbores, wellbores having multiple laterals, and wellbores sharing one or more of these characteristics.

[0074] In **FIG. 3**, treatment intervals **58**, **60** and **62** represent identified intervals of a subterranean formation that have been identified for treatment. In this regard, any

number of intervals or only a portion thereof present in the subterranean formation may be so identified. Alternatively, such intervals may also represent perforated intervals in a cased wellbore. As shown in **FIG. 3**, perforations **66** extend through casing **54** and cement sheath **56** by means known to those of skill in the art, and in doing so form a flow path for fluid from the formation into the casing **54**, and vice-versa.

[0075] The hydrocarbons flowing out of the producing strata in treatment intervals **58**, **60** and **62** through the perforations **66** and into the interior of the casing can be transported to the surface through a production tubing, **64**. Further, and as illustrated in **FIG. 3**, a production packer **68** can be optionally installed substantially near the lower end of the production tubing **64** and above the highest perforation **66** in order to achieve a pressure seal between the production tubing **64** and the casing **54**. Production tubing **64** need not always be used, and in those instances the entire interior volume of casing **54** is used to conduct the hydrocarbons to the surface to wellhead **52**.

[0076] When diversion is needed during a well treatment, diverting agents **72** are used to substantially seal some of the perforations **66**. Substantial sealing occurs when flow through a perforation **66** is significantly reduced, as often indicated by an increase in wellbore pressure as a diverting agent **72** blocks off one or more perforations **66**. In accordance with this aspect of the present invention, diverting agents **72** are preferred to be substantially spherical in shape, although other geometries can be used. Using diverting agents **72** of the present invention to plug some of the perforations **66** is accomplished by introducing the diverting agents **72** into the casing **12** at a pre-determined time during the treatment. When the diverting agents **72** are introduced into the fluid upstream of the perforated parts (**66**) of the casing **12**, they are carried down the production tubing **64** or casing **12** by a flowing fracturing fluid **70**. Once the fracturing fluid **70** arrives at the perforated interval in the casing, it flows outwardly through perforations **66** and into the treatment intervals **58**, **60**, and **62** being treated. The flow of the fracturing fluid **70** through the perforations **66** carries the diverting agents **72** toward the perforations **66**, causing them to seat on the perforations **66**. Once seated on the perforations **66**, diverting agents **72** are held onto the perforations **66** by the fluid pressure differential which exists between the inside of the casing **54** and the treatment intervals **58**, **60** and **62** on the outside of casing **54**. The diverting agents **72** are preferentially sized to substantially seal the perforations **66** when seated upon them. The seated diverting agents **72** thereby serve to effectively close those perforations **66** until such time as the pressure differential is reversed and the diverting agents released, or the diverting agents **72** dissolve over a period of time due to changes in their environment (e.g., the introduction of water).

[0077] The diverting agents **72** will tend to first seal the perforations **66** through which the fracturing fluid **70** is flowing most rapidly. The preferential closing of the high flow rate perforations **66** tends to equalize treatment of the treatment intervals **58**, **60** and **62** over the entire, perforated interval. For maximum effectiveness in seating on perforations **66**, the diverting agents **72** should have a density less than the density of the treating fluid **70** in the wellbore at the temperature and pressure conditions encountered in the perforated area downhole. Generally, and in accordance with this aspect of the present invention, the diverting agent **72**

will have at least a substantial outer surface comprised of collagen or a mixture of collagens. The number of diverting agents **72** needed during a workover or well treatment depends upon the objectives and characteristics of the individual well and the stimulation treatment to be used, and can be determined by one skilled in the art.

[0078] In the practice of disclosed methods, the diverting agent or medium suitable for achieving diversion of fluids into the identified treatment intervals that is employed is the diverting agent of the present invention comprising a particulate substrate and a slowly water-soluble collagen outer layer. In one embodiment, a neutrally buoyant variation of this collagen-containing diverting system can be employed, so as to reduce the chance of segregation of the diverting agent and particulate diverting agent carrier fluid. A “neutrally buoyant” diverting system is a system in which a particulate diverting agent is suspended in a carrier fluid having sufficiently close density or specific gravities to result in a mixture in which solid components of the diverting agent do not substantially settle or rise in the system under static conditions. Such segregation can result in, for example, accumulation of diverting agent at one or more locations in the wellbore and sticking of the pipe string within wellbore sections. Furthermore, segregation can result in loss of diversion action due to movement of the diverting agent away from the intervals to be treated. Neutrally buoyant diverting systems may be of particular advantage in highly deviated or horizontal wells, where gravity segregation of a non-neutrally buoyant diverting system may prevent efficient blockage or reduction in permeability of the entire circumference of formation face exposed in the wellbore due, for example, to migration of diverting agent upwards or downwards in the highly deviated or horizontal section of the wellbore.

[0079] Diverting agents which may be employed include the diverting agents of the present invention, having a slowly water-soluble outer coating, alone or in combination with any diverting agent (e.g., oil soluble, acid soluble, etc.) suitable for diverting subsequent treatment fluids into intervals having lower injectivity. One suitable diverting agent in accordance with the present invention is a diverting agent that is substantially collagen. Examples of suitable diverting agents which can be combined with the diverting agent of the present invention include, but are not limited to, benzoic acid flakes, wax (such as “Divert VI” available from BJ Services), cement grade gilsonite or unitaite, polymers (including, but not limited to, natural polymers such as guar, or synthetic polymers such as polyacrylate), rock salt, and the like. Other types of suitable diverting agents that can be employed include, but are not limited to, acid soluble diverting agents such as those described in U.S. Pat. No. 3,353,874, and phthalimide particles such as those as described in U.S. Pat. No. 4,444,264.

[0080] In one embodiment of the present invention, any type of carrier fluid having a density suitable for forming a neutrally buoyant diverter system may be employed, including natural or synthetic brines (such as KCl water, etc.) and carrier fluids including gelling agents (such as normal or synthetic polymers) or other weighting materials known in the art. Cement grade gilsonite (also known as “Unitate”) is a natural variety of asphalt that is crushed and sorted into multiple-size particles. This diverting agent composition may be blended at the well site with specific chemically-

modified fresh water (water containing for example, about 0.05% to about 1% of a wetting surfactant) to disperse the gilsonite and optionally, a weighting agent (including but not limited to salts such as KCl, NH_4Cl , NaCl, CaCl_2 , etc.) for density adjustment and/or formation-clay control, and a gelling agent (a polymer such as guar gum, hydroxy propylguar, carboxy methylhydroxy propylguar, carboxy methyl hydroxyethyl cellulose, xanthan gum, carboxy methyl cellulose, etc.) for viscosity adjustment and/or drag reduction.

[0081] The diverting agent of the present invention is preferably present in the carrier fluid in concentrations of from about 0.001 pounds per gallon to about 10 pounds per gallon of carrier liquid but concentrations outside this range can also be used. The most preferred concentrations of diverting agents are from about 0.01 to about 6 pounds per gallon of carrier fluid. Diverting agent concentrations of less than about 0.001 pound per gallon will not as readily plug formations when used in carrier fluids volumes which are normally available at an oil well site. A progressively large volume of carrier fluid would be required to create adequate formation plugs at concentrations of less than 0.001 pounds per gallon.

[0082] Concentrations of diverting agent greater than about 10 pounds per gallon would not increase the diverting of the treating fluid to an appreciable extent and therefore are not particularly desirable in carrying out the present invention.

[0083] The carrier liquid is typically composed of water, brine, aqueous acid solutions, or gelled acid solutions. The acid solutions can be gelled with a celluloses, gums, polysaccharides, polyacrylamides, alkoxylated fatty amines and mixtures thereof.

[0084] The diverting agent may be added to the carrier fluid as the treatment is started, continuously as the treating fluid is pumped into the well bore or may be added in intervals in the carrier fluid between stages of the treatment. For instance, in acidizing procedures the diverting agent may be added to the acidizing fluid continuously. Thus, the diverting agent will progressively plug portions of the formation being treated, thereby frustrating the tendency of the acid to flow only into the most permeable portions of the formation and, instead, creating an evenly acidized formation. When the treating fluid is pumped in stages, the first stage is followed by a volume of the diverting material composed of a carrier fluid, usually gelled or emulsified water or acid, containing the bridging agent. The diverting agent seals off the portion of the formation penetrated by the first stage of treating fluid. The second stage of treating fluid is then pumped into another portion of the formation. Alternating volumes of treating fluid and diverting material may be continued to provide a uniformly acidized formation. Although the same technique of continuously introducing the diverting agent in the carrier fluid may be used for fracturing treatments, it is usual for the diverting agent to be added to the carrier fluid in slugs during fracturing operations.

[0085] A fracturing liquid is known to preferentially flow into the portion of the subterranean formation which most readily accepts the liquid. After this portion of the formation is fractured, the bridging agent may be added to the fracturing liquid so that it will plug the already fractured portion

of the formation. Because the fracturing fluid is preferentially flowing into the fracture zone, it will carry the bridging agent with it. The fractured zone is thereby plugged and the fracturing fluid is diverted to the most permeable portion of the formation that is still accepting fluids.

[0086] This method of fracturing and diverting can, in one aspect of the present invention, be repeated to obtain multiple fractures.

[0087] The diverting agent is removed from the formation by means of sublimation of the diverting agent or by solubilization of the diverting agent by the produced fluids. Increasing formation temperatures result in a greater rate of dissolution or sublimation of the diverting agent. For instance, it has been found that at about 250° F., approximately 80 percent by weight of the slightly water-soluble collagen sublimates in 24 hours, while at 300° F., about 95 percent by weight sublimates in 24 hours, and at a temperature of about 400° F., about 99% of the slightly water-soluble collagen sublimates/dissolves in about 24 hours. This shows that the rate of sublimation/dissolution of the diverting agent increases with increasing formation temperature.

[0088] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the invention.

Examples

Example 1

Prophetic Example

[0089] The following prophetic example describes a method of how the soluble coating on the propping agent or agents of the present invention can be used to divert fracture growth and extend the fractures into the productive zone of an oil or gas well. The primary purpose of the soluble coated proppant is to define an upper and lower boundary in the hydraulically generated vertical fracture so that the main direction of growth continues to extend outward in length away from the wellbore. This additional length of the conductive fracture aids in draining additional areas of the productive formation, allowing oil, gas, and/or water recovery production to be improved and greater flow rates to be established as a result of longer fracture length.

[0090] The following steps can be followed, using the soluble coated proppant materials of the present invention.

[0091] 1. A fracture injection rate is established with a low viscosity fracturing fluid.

[0092] 2. A soluble coated proppant, such as walnut hulls coated with a cross-linked collagen, bauxite coated with cross-linked collagen, or a combination of both, is added at the blender tub in order to form a slurry in the fracturing fluid.

[0093] 3. The fracturing fluid containing the soluble coated proppant is pumped downhole.

[0094] The first part of the slurry enters the initial crack, taking the most fluid. In doing so, it slowly plugs the borders of the created fracture due to the use of a soluble diverting agent, such as collagen, that slowly softens and swells in the fluid.

[0095] 4. Once the flow rate is slowed or substantially reduced in the first crack, pressure builds up until another flow path, crack, or zone begins to take the soluble coated proppant-containing slurry.

[0096] 5. In the instance that both the top and the bottom of the fracture need to be contained by the soluble coated proppant, two different proppant densities are preferably used. For example, a high density bauxite particle is coated with a soluble, collagen coating that slowly softens and swells as it falls in the fracture to the bottom of the vertically-created fracture. To slow the growth upwards in the vertical fracture, a second proppant of low density, such as a soluble-coated walnut hull, is added to the injection fluid. As the injection fluid enters the formation, the low-density, soluble-material coated proppant rises in the vertical fracture and slows down fluid loss and growth in an upward direction.

[0097] 6. As the fracture is still being injected with fluid above the fracture rate and pressure, the fracture continues to grow away from the wellbore and control of the fracture growth is maintained by controlling the flow rate of the fracturing fluid. Injection is continued until the regular proppant fills the fracture, pressure reaches a pre-set limit, or until the total planned volume is injected.

[0098] 7. Standard, non-soluble coated proppants, such as Ottawa Sand (20/40), ceramic, or any number of resin-coated proppants, are injected into the formation, once the top and bottom growth is diminished. Pumping is continued until the full amount of designated proppant (or proppants) are placed in the created fractures.

[0099] 8. The well is shut in, and the pumping equipment is removed.

[0100] 9. The well is returned to production, and the soluble collagen-coating on the walnut hulls or bauxite is removed as the water in the formation dissolves the soluble coating on the proppant over time.

Example 2

Procedure for determining the rate and degree of polymer dissolution

[0101] Sand substrate was coated with various water-soluble polymers:

Chemical Name	Trade Name	Supplier
Poly(ethylene) oxide	WSR 80	Dow Chemicals
Poly(propylene) oxide	WSRN 750	Dow Chemicals
Poly(propylene) oxide	UCAR309	Dow Chemicals
Poly(lactic acid)	PLA6551-D	E&M specialties
Poly(lactic acid)	PLA5600	E&M specialties
Poly(vinylacetate/alcohol)	PVA/Hydrolene	Idroplax Inc.

-continued

Chemical Name	Trade Name	Supplier
Collagen 1	Glue 512	Milligans and Higgins
Collagen 2	GM Bond	Hormel foods

[0102] Thereafter, the following test procedure was used to determine rate and degree of solubility:

[0103] Determine the total mass of the polymer on the sand by regular LOI procedure. Add 500 grams of coated sand in 1 liter of water. Take a 400 mm filter paper and weight it on an analytical balance up to 4 decimal places. Prepare vacuum filtration apparatus by using 400 mm filter paper, perforated ceramic funnel, 2 liters Erlenmeyer flask with side opening connected to the vacuum pump by a rubber tube. Filter the coated sand and water slurry through 400 mm filter paper after each one-minute interval. Remember to add coated sand back in the "filtered" water. Remove the filter paper from the perforated funnel after filtration is complete, and allow it to dry by keeping it in desiccators. Weigh the filter paper. This is the combined weight of dissolved polymer and filter paper, and thus it should be greater than the weight of the filter paper before it was used in filtration process. Calculate the % of dissolved polymer by using the following formula:

$$X=((C-B)/A)\times 100$$

[0104] Where,

[0105] X=the percentage of dissolved polymer

[0106] A=mass (gms) of the polymer on the sand grains

[0107] B=mass (gms) of the filter prior to filtration process

[0108] C=mass (gms) of the filter after filtration process

Particles that swell and then dissolve	Particles that dissolve without swelling
UCAR309	WSR 80
COLLAGEN 1	WSRN750
COLLAGEN 2	PLA 6551-D
	PLA 5600

[0109] The results of this test procedure were that a polyethylene oxide(WSR 80 from Dow Chemical) reach full dissolution at 80° F. in about 300 minutes, at 150° F. it required about 180 minutes, and at 200° F. it required about 90 minutes.

[0110] The same test was run using another polymer. These results showed that the polypropylene oxide polymer-(WSRN 750 from Dow Chemicals) reached full dissolution at 80° F. in about 390 minutes, at 150° F. it required about 320 minutes, and at 200° F. it required about 245 minutes to fully dissolve.

[0111] Polymers that swell show 100% solubility within 30 minutes, but microscopic analysis shows retention on the filter paper due to swelling instead of dissolution. Formation

of gelatinous mass and noticeable increase in the volume of the sand/water slurry indicate polymer swelling instead of polymer dissolution.

[0112] All of the compositions, methods, and/or processes disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions, methods, and/or processes and in the steps or in the sequence of steps of the methods described herein without departing from the concept and scope of the invention. More specifically, it will be apparent that certain agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the invention.

What is claimed is:

1. A diverting material comprising:
a particulate substrate; and
a water-soluble polymer coating,
wherein the water-soluble polymer coating forms a substantial outer coating on the particulate substrate.
2. The diverting material of claim 1, wherein the particulate substrate is selected from the group consisting of natural materials, silica proppants, ceramic proppants, metallic proppants, synthetic organic proppants, and mixtures thereof.
3. The diverting material of claim 1, wherein the particulate substrate is a resin coated proppant.
4. The diverting material of claim 1, wherein the water-soluble polymer is collagen, poly(alkylene) oxide, poly(lactic acid), polyvinylacetate, polyvinylalcohol, polylactone, polyacrylate, latex, polyester, periodic chart elements of group I or II (alkali metal or alkaline earth metal) silicate polymers or admixtures thereof.
5. The diverting material of claim 1, wherein the particulate substrate has a particle size of from about 3 mesh to about 200 mesh.
6. The diverting material of claim 4, wherein the collagen is Type I collagen, Type II collagen, Type III collagen, Type IV collagen, or Type V collagen.
7. The diverting material of claim 4, wherein the water-soluble collagen is crosslinked with a cross-linking agent selected from the group consisting of aldehydes, carbodiimides, isocyanates, and acyl azides.
8. The diverting material of claim 1, further comprising a non-water-soluble polymer in combination with the water-soluble polymer coating.
9. The diverting material of claim 8, wherein the non water-soluble polymer is phenol-aldehyde novolac polymers and phenol-aldehyde resole polymers.
10. The diverting material of claim 1, wherein the water-soluble polymer is poly(alkylene) oxide, poly(lactic acid), polyvinylacetate, polyvinylalcohol, polyvinylacetate/polyvinylalcohol graft polymers or admixtures thereof.
11. The diverting material of claim 10, wherein the poly(alkylene) oxide is poly(ethylene) oxide, poly(propylene) oxide, poly(ethylene oxide)-poly(propylene oxide) block copolymers, or mixtures thereof.

12. A diverting fluid for diverting oil well treating liquids to progressively less permeable portions of a subterranean formation, said fluid comprising:

an aqueous carrier liquid having dispersed therein particulate diverting material of any one of claims 1-11.

13. The diverting fluid of claim 12, wherein the particulate diverting material comprises varying densities greater or less than the density of the carrier fluid.

14. The diverting fluid of claim 12, wherein the diverting material is present in the carrier liquid in an amount from about 0.001 pounds per gallon to about 10 pounds per gallon of the carrier liquid.

15. The diverting fluid of claim 12, wherein the carrier liquid is water, brine, aqueous acid solutions, or gelled acid solutions.

16. A method of treating a subterranean formation during fracturing treatment so as to increase the stimulation of the subterranean formation, the method comprising:

pumping into the subterranean formation a diverting fluid of any one of claims 12-15;

allowing the carrier liquid to permeate into the formation so as to carry the diverting material into the subterranean formation; and

allowing the diverting material to plug porous portions of the formations thereby diverting flow of treating fluid to less permeable portions of the formation.

17. The method of claim 16, wherein the formation has a temperature from about 75° F. to about 400° F.

18. The method of claim 16, wherein the treating of the subterranean formation is a fracturing treatment, and wherein the stimulation increased is the length of the fractures.

19. A method treating a cased wellbore to divert flow of fluids from one zone to another, the method comprising:

pumping into said wellbore a diverting fluid comprising an aqueous carrier liquid having dispersed therein a particulate form of a water soluble polymer, wherein the particulate polymer has a density greater than or less than the density of the carrier liquid;

allowing the particulate polymer to divert flow of a treating fluid from one zone to another.

20. The method of claim 19, wherein the treating fluid is diverted to flow into a zone of higher pore pressure or lower permeability.

21. The method of claim 19, wherein the wellbore has a temperature from about 75° F. to about 400° F.

22. The method of claim 19, wherein the water-soluble polymer is collagen, poly(alkylene) oxide, poly(lactic acid), polyvinylacetate, polyvinylalcohol, polylactone, polyacrylate, latex, polyester, polyvinylacetate/polyvinylalcohol graft polymer, periodic chart elements of group I or II (alkali metal or alkaline earth metal) silicate polymer, or mixtures thereof.

23. The method of claim 19, wherein the particulate polymer has a particle size of from about 3 mesh to about 70 mesh.

24. The method of claim 22, wherein the poly(alkylene) oxide is poly(ethylene) oxide, poly(propylene) oxide, poly(ethylene oxide)-poly(propylene oxide) block copolymers, or mixtures thereof.

25. The method of claim 19, wherein the particulate polymer is comprised of varying densities greater or less than the density of the carrier fluid.

26. The method of claim 19, wherein the particulate polymer is present in the carrier liquid in an amount from about 0.001 pounds per gallon to about 10 pounds per gallon of the carrier liquid.

27. The method of claim 19, wherein the carrier liquid is water, brine, aqueous acid solutions, or gelled acid solutions.

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