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(54) Title: DESTRUCTIBLE CONTAINERS FOR DOWNHOLE MATERIAL AND CHEMICAL DELIVERY

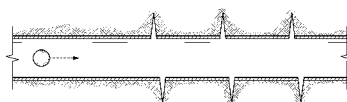


FIG. 1A

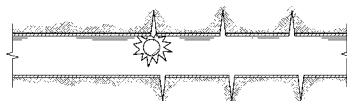


FIG. 1B

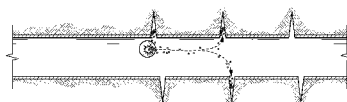


FIG. 1C

(57) Abstract: A method of treating a downhole region penetrated by a wellbore with a treatment agent is given, including delivering the treatment agent to the wellsite enclosed in one or more destructible containers, inserting the one or more destructible containers into the fluid being pumped down the well, and mechanically breaking the one or more destructible containers in the wellbore or in the formation to release the treatment agent. A method is also given for treating a downhole region penetrated by a wellbore with a special solid diverting material, which includes special shapes such as fibers or flakes and/or blends of specially sized particles, including delivering the special solid diverting material to the wellsite enclosed in one or more containers, inserting the one or more containers into fluid being pumped down the well, and allowing the one or more containers to release the special solid diverting material in the wellbore.





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DESTRUCTIBLE CONTAINERS FOR DOWNHOLE MATERIAL AND CHEMICAL DELIVERY

Background

Drilling, cementing, stimulation, and various treatments, including workover operations, of oil and gas wells frequently require using various chemical additives. In some situations it is necessary to deliver such chemical additives downhole while minimizing their interactions with wellbore fluids or the wellbore itself.

An example of a need to deliver materials downhole without interaction with the injection fluid is the use of slugs of fiber-containing slurries for fracture isolation. Treatments, for example of horizontal oil and gas wells as well as multi-layered formations, frequently require using diverting techniques in order to enable treatment redirection between different zones. Diverting methods include, but are not limited to, using mechanical isolation devices such as packers and wellbore plugs, setting bridge plugs, pumping ball sealers, pumping slurried benzoic acid flakes and pumping removable and/or degradable particulates. Fracture isolation with fibers is achieved by initial bridging of fibers inside the fracture, which results in plug formation by accumulation of the rest of the fiber material (and other solids if present) on the bridge formed. Initiation of fiber bridging depends on the fiber concentration, so fracture isolation by this method is very sensitive to the degree of dilution of the fiber slurry with wellbore fluid during injection, which is difficult to control. Similarly, treatment diversion with particulates is typically based on bridging of particles of the diverting material behind the casing and forming a plug by accumulating the rest of the particles at the bridge formed. Two typical problems related to treatment diversion with particulate materials are that 1) there may be reduced bridging ability of the diverting slurry during pumping resulting from dilution of the slurry by the wellbore fluid (because of interface mixing), and 2) when mixtures of particle sizes are used, there may be particle separation by size or other parameters during pumping which results in the formation of more permeable plugs and poorer treatment diversion. Excessive volumes of diverting slurry typically must be pumped to minimize these effects, which increase costs and also result in a significant increase in the risk of wellbore plugging by the excess diverting material. A method of delivery of a slurry that minimizes slurry dilution or alteration during injection would be valuable.

An example of the need to deliver chemicals downhole without their interaction with the wellbore is delivery of acid for zonal stimulation. Usually such treatments carry a risk of casing damage because of the potential reaction of the casing with acid. To overcome this problem, acid retarders, which slow down the reaction of the acid with metal, are introduced into the pumping fluid. Such retarders are not always effective and full casing protection is difficult to achieve. A method of delivering acid to the bottom of a well without acid interaction with the wellbore would be desirable.

Summary

One embodiment is a method of treating a downhole region penetrated by a wellbore with a treatment agent. The method includes delivering the treatment agent to the wellsite enclosed in one or more destructible containers, each having a shell, inserting the one or more destructible containers into the fluid being pumped down the well, and mechanically breaking the shell of the one or more destructible containers in the wellbore or in the formation to release the treatment agent. The one or more destructible containers may be made of one or more materials. At least one of the materials making up the one or more destructible containers may be degradable. At least a portion of the treatment agent may also be degradable. The breaking of the destructible container may be promoted by at least partial dissolution of the shell of the container in the wellbore fluid. The treatment agent may be in the form of a slurry inside the one or more destructible containers. The one or more destructible containers may include one or more fluid flow paths allowing entry of wellbore fluid into the container. When the wellbore is cased and the casing is perforated, and the smallest dimension of the one or more destructible containers is larger than the diameter of the perforations, the one or more destructible containers may be mechanically destroyed by contact with one or more perforations. A restriction may be placed in the wellbore to break the one or more destructible containers at a desired location; the restriction has an opening smaller than the smallest dimension of the one or more destructible containers. Optionally, more than one restriction may be placed in the wellbore, said restrictions successively smaller the farther away from the surface. The container also may break when a fracture or wormhole in a formation

becomes smaller than the container. The one or more destructible containers may be made by shrink wrapping one or more films around the treatment agent. The one or more destructible containers may have a hollow shell into which the treatment agent is placed. The shell of the one or more destructible containers may be made of polyvinyl alcohol or gelatin. A plurality of destructible containers may be used and the destructible containers may vary in one or more of size, composition, or contents.

Another embodiment is a method of treating a downhole region penetrated by a wellbore with a special solid diverting material. The method includes delivering the special solid diverting material to the wellsite enclosed in one or more containers, each having a shell, inserting the one or more containers into fluid being pumped down the well, and allowing the one or more containers to release the special solid diverting material in the wellbore. The one or more containers may be made of one or more materials. At least one of the materials making up the one or more containers is generally at least partially degradable. At least a portion of the special solid diverting material may be degradable. At least a portion of the special solid diverting material may include a blend of particles having at least three distinct sizes. At least a portion of the special solid diverting material may include one or more of fibers, fiber flocks, fibrillated fibers, ribbons, flakes or platelets. The special solid diverting material may be in the form of a slurry inside the container. The one or more containers may include one or more fluid flow paths allowing entry of wellbore fluid into the container. The release of the special solid diverting material may be by mechanical destruction of the container. The release of the special solid diverting material may be promoted by a chemical that reacts with the container. The release of the special solid diverting material may be promoted by dissolution of the container's shell in the wellbore fluid. The one or more containers may be made by shrink wrapping one or more films around the special solid diverting material. The one or more containers may include a hollow shell into which the special solid diverting material is placed. The shell of the one or more containers may be made of polyvinyl alcohol or gelatin. A plurality of containers may be used and the containers may vary in one or more of size, composition, or contents.

Yet another embodiment is a system for delivery of a special solid diverting material to a downhole location without dilution or separation of special solid

diverting material components; this system includes the special solid diverting material enclosed in one or more destructible containers. The one or more destructible containers may be made of one or more materials. At least one of the materials making up the one or more containers may be degradable. The one or more destructible containers may include one or more fluid flow paths. The special solid diverting material may be in the form of a slurry inside the one or more destructible containers. The one or more destructible containers may be mechanically destructible. At least a portion of the special solid diverting material may be degradable. The one or more destructible containers may be made by shrink wrapping one or more films around the special solid diverting material. The one or more destructible containers may include a hollow shell into which the special solid diverting material is placed. The one or more destructible containers may be made of a shell made of polyvinyl alcohol or gelatin. A plurality of destructible containers may be used and the destructible containers may vary in one or more of size, composition, or contents.

Brief Description of the Drawings

Figure 1 is a schematic of destruction of a destructible container at a perforation.

Figure 2 is a schematic of destruction of a destructible container at a restriction apparatus placed in a wellbore.

Figure 3 is a schematic of the destruction of a container having a dissolvable shell in a wellbore.

Figure 4 is a schematic of one device for introducing destructible containers into a high pressure flow line.

Figure 5 shows a schematic of the experimental apparatus for studying the release of particulate materials from destructible containers at perforations.

Detailed Description

The description and examples are presented solely for the purpose of illustrating some embodiments and should not be construed as a limitation to the scope and applicability. Although some of the following discussion emphasizes

diversion in fracturing, the destructible container and method may be used in many other wellbore operations. Some embodiments shall be described in terms of treatment of horizontal wells, but are equally applicable to wells of any orientation. Some embodiments shall be described for hydrocarbon production wells, but it is to be understood that they may be used for wells for production of other fluids, such as water or carbon dioxide, or, for example, for injection or storage wells. It should also be understood that throughout this specification, when a concentration or amount range is described as being useful, or suitable, or the like, it is intended that any and every concentration or amount within the range, including the end points, is to be considered as having been stated. Furthermore, each numerical value should be read once as modified by the term “about” (unless already expressly so modified) and then read again as not to be so modified unless otherwise stated in context. For example, “a range of from 1 to 10” is to be read as indicating each and every possible number along the continuum between about 1 and about 10. In other words, when a certain range is expressed, even if only a few specific data points are explicitly identified or referred to within the range, or even when no data points are referred to within the range, it is to be understood that the inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that the inventors have possession of the entire range and all points within the range.

We have devised destructible containers for chemicals and materials and devised a method of using these destructible containers for downhole delivery of chemical and material treatment agents. The method comprises introducing the destructible containers containing chemicals or materials into the pumping line or into the wellbore followed by bullheading the containers and their contents downhole. The destructible containers minimize the risk of interaction of the chemicals or materials with wellbore fluid or with the wellbore itself until destruction of the containers, which may occur, for example:

- at the surface during introduction into the pumping line or wellhead,
- along the wellbore during downhole delivery,
- at a specific location in the wellbore, and/or
- at bottomhole.

Note that in all these situations, destruction occurs before the containers can enter the formation surrounding the wellbore. The destructible container comprises a shell holding one or more treatment agents. The shell separates the treatment agent or agents from the outside environment until the shell is destroyed, although if, desired a small amount of an outside fluid may be allowed to enter the shell before destruction of the shell. The shell may also be defined as a chemical or physical barrier or bond, including some form of adhesion of particles and/or fibers due to interaction of a coating on the surface of the materials, holding chemicals and/or materials in a pre-defined volume until it is intended to expand the contents beyond the confines of the designed volume. The shell may have various mechanical properties and may be, for example, rigid, flexible, elastic, hard, fragile, or not fragile. Destruction of the containers may be brought about by mechanical destruction, chemical action, dissolution or thermal destruction. When the destruction is by a mechanical action, then it is preferred that the remains of the empty, or nearly empty, container be subsequently destroyed in the wellbore or in the near wellbore region by chemical action, dissolution or thermal destruction. The treatment agent may be any chemical or particulate materials used in wellbores and formations, such as, but not limited to, fluid loss additives, pH changing agents, lost circulation materials, scale solvers, cross linking agents, oxidizers, sealing agents, diverting agents, viscosifying agents, fibers, fluid breakers and viscosity reducing additives, clean-up additives, surfactants, rigid gels, chemical plugs, salts, and chemicals that react exothermically. Note that the treatment agent in the shell may be only part of a final chemical or physical process in the well. For example, the treatment agent may be a crosslinker that reacts with polymer that was not in the destructible container to form a gel that performs some treatment in the well. In addition, treatment agents inside the shell, including diverting agents, may be coated, for example with a resin, a polymer, a salt, an organic compound, and/or an inorganic compound.

We have in particular found a method of using these destructible downhole containers and their contents for treatment diversion during stimulation operations for zonal isolation and/or for changing the injection profile of a treating fluid into the formation when several perforated zones are treated in one stage. For diversion, the destructible container consists of a destructible enclosure or shell filled with a diverting material, preferably a diverting material that is partially or completely

degradable, soluble, reactible, meltable or otherwise destroyable other than mechanically. Optionally, the degradation may be caused or enhanced by a chemical inside the destructible container, for example in addition to the main treatment agent. Optionally, shell destruction optionally may be initiated by penetration of the wellbore fluid into the container (as examples, a water-soluble enzyme breaker placed inside a container having a gelatin shell; citric acid placed inside a container having an acid-soluble or acid-destructible shell such as one made of borate cross-linked guar or cellulose; or solids such as NaOH, $\text{Ca}(\text{OH})_2$, CaCO_3 or $\text{Mg}(\text{OH})_2$ included in the contents of a polylactic acid shell). In describing a diverting material as being at least partially destroyable or degradable we mean that the diverting material, or at least one component of the diverting material is sufficiently destroyable or degradable that the ability of the plug or seal to block fluid flow is reduced so that it no longer blocks fluid flow; in some cases this may be as little as about 5 percent of the diverting material being destroyable or degradable. The container, whose shell protects the contents from dilution with wellbore fluids as well as from particle size and/or shape separation during pumping, is introduced into the wellbore and pumped downhole. The container is destroyed, for example mechanically, causing the release of the diverting material which plugs or seals a stimulated interval and provides treatment diversion to another region. Several preferred mechanisms may be used for enclosure or shell destruction:

- shear and/or mechanical collisions in the wellbore,
- differential pressure attempting to force the container through perforations, and/or
- destruction by a downhole apparatus, for example a restriction, specially set in the wellbore for this purpose.

As is usually desired, removal of the diverting material as well as shell components is preferably achieved by self-degradation under downhole conditions; by introduction of special chemical agents, such as solvents, especially under dynamic underbalanced conditions; or by specialized wellbore intervention (for examples hydrojet cleaning, solvent cleaning, and using a downhole heater).

Optionally, the container may be destroyed sufficiently by at least partial dissolution (for example more than 5% of the shell being dissolved) in the surrounding fluid (for example a polyvinyl alcohol shell), or by weakening of the shell by partial dissolution in the surrounding fluid followed by mechanical destruction (for example a gelatin shell).

Using destructible containers for fiber and/or particle delivery for fracture isolation allows maintenance of high fiber and/or particle concentrations at the downhole location by minimizing the risk of dilution of the fibers with wellbore fluid. The fiber and/or particles in the destructible containers may be dried or slurried. The liquid in which the solids are slurried may be, for example, an aqueous liquid or a linear or crosslinked aqueous polymer solution. In one specific embodiment the solids may be slurried *in situ* in a wellbore fluid which penetrates the container. The liquid phase of the slurry may also be non-aqueous, such as an alcohol (as examples glycerol, ethanol, methanol, and isopropanol, ethylene glycol); and/or liquid hydrocarbons such as diesel, hexane, or aromatic hydrocarbons such as benzene, toluene etc. Delivery of acid in such containers with subsequent acid release of the acid downhole provides casing or wellbore wall protection during acid treatments. Other treatment agents may be delivered advantageously, for example bases such as sodium hydroxide.

Furthermore, using particle or fiber-holding destructible containers significantly simplifies wellsite delivery of those or other container contents. Problems with existing methods of fiber and/or particle delivery based on using screw feeders include, but are not limited to, metering difficulties and plugging of equipment. Wellsite delivery of special solid diverting materials, such as fibers and/or particles, in destructible containers solves these problems, because such containers may be introduced into the treating fluid with the same techniques as commonly used for proppant or any solid or particulate material. In one embodiment fibers and/or particulates are vacuum packed into small bundles (to maximize the concentration) and surrounded by a coating or put into an enclosure, for example shrink-wrapped or vacuum packed, that is engineered to have various degradation times or destruction degrees of difficulty. Alternatively, an additive is used at various concentrations to interact with the coating or container at varying rates. In one specific example, where

the container's principal purposes are wellsite delivery and metering, and it is not necessary to minimize dilution or separation of the contents as they travel downhole, such a shell or coating may optionally quickly be degraded or destroyed after introduction of fiber (or other shape) and/or particle packs into the treating fluid so that fiber (or other shape) and/or particle dispersion occurs in the mixing and/or pumping equipment or while traveling downhole. This method may still deliver higher concentrations of special solid diverting materials to a location downhole.

It should be noted that using small (for example from about 1 mm to about 100 mm, especially from about 1 mm to about 70 mm, and most especially from about 1 mm to about 20 mm) containers for fibers or other shapes simplifies fiber (or other shapes) delivery. These containers may be introduced through a blender in large amounts and simple equipment may be used. Premature destruction of some of the containers in the treating equipment is not critical as long as the majority (for example at least about 60 %) of the containers survive to enter the wellbore. Note that if a container is made of multiple layers, it is not considered destroyed until all of the layers have been destroyed to the point that the contents can be released. The ultimate fiber concentration that can reliably be obtained downhole is much higher than if fibers are fed directly into the fluid.

The following discussion of possible alternatives merely provides context information related to the disclosure and may not constitute prior art. The inventors are not aware of any method of wellsite delivery of solid materials useful for fluid flow diversion that utilizes mechanically destructible containers which are destroyed in surface equipment and/or which are bullheaded downhole and destroyed in the wellbore by any means before entering a formation. The inventors are not aware of any method of downhole delivery of any chemical agents or solid materials that are placed in destructible containers that are pre-formed empty and then filled, or are placed around the agents or materials, and then broken in surface equipment or in the wellbore by special apparatus previously placed in the wellbore or by perforations to release the contents into a formation or fracture, such as but not limited to, bags or hollow balls (that may optionally be rigid and may optionally dissolve, degrade, etc. after release of the contents). U.S. Pat. No. 7,049,272 discloses a method of treating a well with solids, liquids or apparatuses by 1) encasing said solids, liquids or

apparatuses in a pre-formed water soluble shell such as a PVA cylinder, 2) conveying said encased solids, liquids or apparatuses to a predetermined location in the well, and 3) allowing the water-soluble shell to dissolve in the aqueous phase in the wellbore. The shell is "resistant to diffusion in either direction" and "able to resist substantial physical and mechanical forces without breaking"; illustrative examples include placing encased soap at the bottom of the well for assisting in gas-lift, and placing corrosion inhibitors. No action is taken to destroy the shell and the shell does not release any material before it reaches the treatment location. There are several applications in the oil-field industry which are based on using encapsulated chemicals for delayed triggering of chemical reactions downhole. U. S. Pat. No. 6,794,340 discloses a method of removing drill cuttings from wellbores and drilling fluids by crosslinking drilling fluid with a crosslinker and a crosslinker activator that is encapsulated and released by destruction of the capsule as it passes through the drill bit or that is released by dissolution or melting of the encapsulation material. All encapsulated material and any remaining encapsulation material are returned to the surface. U. S. Pat. No. 4,614,599 discloses a lost circulation treatment comprising encapsulating lime in a reaction-preventive protective casing (such as a film of wax) in a circulating drilling fluid to prevent the lime from reacting with clays in the borehole until it is desired to breach the casing; if lost circulation occurs, circulation is slowed or stopped so that the temperature rises and the time of the fluid in the lost circulation pathway lengthens and the coating dissolves or melts and the lime reacts with clays in the drilling fluid and/or the formation to plug the lost circulation pathway. Using encapsulated liquids for formation treatments is disclosed in U.S. Pat. No. 6,761,220 in which contents of capsules "within the downhole region of a well" may be released by crushing, rupturing, dissolving, diffusion of fluid through, or melting of, the capsule. U. S. Pat. No. 6,924,253 discloses release of encapsulated ionic liquids for scale removal in the wellbore or near wellbore region. Encapsulated chemicals, other than diverting solids, for downhole or in-formation release for various treatments, such as gel breakers for hydraulic fracturing, are known; breaker release in the fracture after leaving the wellbore is activated by temperature or by crushing capsules during fracture closure. Capsules may also degrade in the wellbore or formation, or dissolve, or melt, or be ruptured by entrance of a fluid by osmosis. There are also downhole tools that can be controlled to release active chemicals.

Some are integrated into the casing where transferring the internal fluid from the reservoir relies on the Venturi effect. Others are wireline or string conveyed apparatuses; release of chemicals is activated from the surface after positioning the apparatuses at the desired location. Other diversion methods include but are not limited to diversion with 1) viscous fluids or fluids that become viscous, such as the so-called self-diverting fluids, 2) foams and emulsions, 3) ball sealers, including degradable and soluble ball sealers, 4) mechanical tools and well completion tools, 5) limited entry perforation diverting techniques, and 6) stress assisted diversion.

In one embodiment, the destructible containers are made of a material that is at least partially degradable, soluble, reactible, meltable or otherwise destroyable other than mechanically, or are made of more than one component, at least one of which is destroyable other than mechanically, so that after destruction at least part of the container will disappear. In describing a container as at least partially destroyable or degradable we mean that at least 5 %, preferably at least 50 %, of the container is destroyable or degradable.

For wellsite delivery of the proposed destructible containers, existing or modified delivery equipment may be used, depending on the mechanism of the destruction of the containers and the purpose of their use. The location at which the destruction occurs may be determined by selection, adaptation, or special design of surface and/or downhole equipment.

Some embodiments include delivering diverting materials downhole in destructible containers. The principle advantages include 1) delivering the material to a desired location downhole in concentrated form while eliminating or reducing the problems of dilution or size or density separation of the materials before they arrive at the desired downhole location, and 2) convenient delivery to the well site and convenient injection into the injection fluid without the problems associated with transporting and metering materials that may be difficult to handle, such as fibers and mixtures of different sizes of, or different shapes of, materials.

Embodiments may be described here in terms of solid diverting materials in fracturing, but the destructible container can carry any inert or active solids, fluids, or combinations of solids and fluids to any desired downhole location for any purpose. The container is generally either a pre-formed container such as a hollow sphere, for

example of polylactic acid (PLA), or a bag that is filled after it is made or a similar structure that is fashioned around the contained material; either way, it is sealed after it is filled. The container may be referred to as a shell, envelope, etc. The container is then introduced into the fluid being injected downhole, is carried to the desired location, and then is deliberately broken there to release the contents. Except for “special solid diverting material”, by destructible “container” we do not mean a coating of another material that is put on by spray coating or polymerization and the like as is often meant in the literature when a material is described as “encapsulated”. By special solid diverting material we mean, for example, fibers; other shapes such as flakes, platelets, ribbons, rods, precipitated material from chemical reactions, grains, pellets; mixtures of different sizes of approximately spherical materials; and mixtures of fibers or flakes or other shapes and one or more sizes of approximately spherical materials (for example having aspect ratios of less than about 5, preferably less than about 3). Non-limiting examples of approximately spherical materials include plastic beads, sand, ceramic beads, glass, wax beads, proppant, silica flour, alumina, and calcium carbonate. All such special solid diverting materials are designed to plug openings of a certain size, such as a wellbore, a vug, a fluid loss pathway, a hydraulic fracture, wormhole etc. Special solid diverting materials may be enclosed in any way and be within the scope of embodiments. Preferably the special solid diverting material is degradable and/or removable under downhole conditions. Chemicals or materials other than special solid diverting materials enclosed in mechanically destructible containers are within the scope of embodiments.

Figures 1, 2, and 3 show several methods of deliberately breaking destructible containers downhole. In Figure 1, release of diverting material is caused by destruction of downhole containers at perforations. The wellbore is shown as horizontal but may be in any orientation. The container flows along the wellbore (A) and is pressed against the opening of the first perforation it encounters, by the fluid pressure, and the container breaks (B), which is believed to be due to differential pressure across the perforation. The perforations have dimensions smaller than the smallest dimension of the container. Some or all of the container contents passes through the perforation and into the formation; any material that does not pass through the perforation that broke the container is carried further along the wellbore and into one or more subsequently encountered perforations (C).

In Figure 2 the destruction is caused by a special restriction, having a cross section smaller than that of the destructible container that has been placed in the wellbore; the restriction typically is placed upstream of the perforations and has a diameter smaller than the smallest dimension of the container. After the container is broken the contents enter downstream perforations. A variation of this system is the use of varying sizes of destructible containers and several progressively smaller restrictions along the perforated zone. Smaller containers pass through the first, larger, restrictions and do not break until they reach a restriction smaller than the container. This ensures that all the perforations receive treatment material; this scheme can also be used to deliver different materials to different regions of the perforated zone. Not shown is that in these cases the perforations may optionally be larger than at least some of the containers, or alternatively some of the containers may be broken by perforations.

In Figure 3 the destruction is caused by dissolution of the shell of the destructible container as it passes down the wellbore. After the container dissolves or is broken by at least partial dissolution, the contents enter downstream perforations. The container is in the wellbore at [1], and destroyed by at least partial dissolution of the shell by the time it reaches location [2]. The contents [3] are released and displaced into the perforations at location [4].

Alternatively, destruction of the container may be caused by shear downhole in the wellbore (for example at a change in direction or a narrowing of the wellbore), or by passing near or collision with other apparatus downhole such as a perforating gun. Deliberate mechanical destruction may be aided by partial chemical destruction or dissolution or thermal weakening of the shell or by a combination of such processes. Destructible containers may also be sized to break at a certain point inside a fracture or wormhole.

Destructible containers may be tested, preferably in the laboratory, to ensure that they break where desired. For example, if the destructible containers are to be broken by a downhole restriction or by perforations, they may be tested to ensure that they are not broken by high differential pressures encountered first or by striking surface line or wellbore walls (for example at bends). If necessary, the strength of the shell may be increased or holes or a leaf valve or leaf burst valve may be used to

relieve differential pressure. Dissolvable container may be tested by measuring the time required for sufficient destruction of the shell by dissolution at conditions emulating the conditions during pumping (shear rate, temperature, pressure, etc.). The shell is considered to have been destroyed at the point at which, although the shell may not have been completely dissolved, the mechanical integrity has been reduced significantly enough that the contents can be released.

The mechanically destructible downhole container may be of any shape, but is preferably spherical or has an aspect ratio of less than about 3. An approximately spherical shape is advantageous because: (1) if the container is not approximately spherical and one dimension is significantly longer than the others, then the container may become trapped in surface lines or connections if it is not correctly oriented when it enters a connection or pipe; (2) surface handling of spheres is easier than surface handling of non-spherical shapes and the orientation when feeding the container into the well is not an issue; and (3) for spheres, the same equipment, calculations, and considerations established for ball sealers may be used. Those correlations do not apply if container is not spherical. The exact dimensions depend upon the nature of the wellbore, surface equipment, and downhole equipment, but typically, the volume of the destructible downhole containers varies from about 0.5 cm^3 (which corresponds to a sphere having a diameter of about 1 cm), to about 24 L (which corresponds to a cylinder having a diameter of about 17.5 cm and a length of about 100 cm). The preferred volume of the destructible downhole containers ranges from about 8 cm^3 to about 2.8 L (which corresponds to spheres having diameters from about 2.5 cm to about 17.5 cm). The most preferred volume of the destructible downhole containers is in the range of from about 20 cm^3 to about 1 L (which corresponds to spheres having diameters from about 5 cm to about 12.5 cm). When the primary purpose of the containers is wellsite delivery of fiber-based materials, the preferred volume of the containers is in the range of about 0.5 cm^3 and about 2 cm^3 , which allows pumping such containers through typical surface equipment.

The outer enclosure or shell (or bag or envelope, etc.) of the destructible container, which may be rigid or flexible, is made of a material which is mechanically destructible at downhole conditions. Examples of such materials include plastics, glass, ceramics, gelatin etc. The shell of the container in some embodiments may also

be chemically degradable, dissolvable or meltable. Normally, degradation takes place after the shell is broken.

In one embodiment the shell may be degradable in, or soluble in, the wellbore or formation fluids. This minimizes the risk of formation damage by the shell material and assists in wellbore and formation clean-up. Examples of degradable materials which may be used for making the shell of the destructible downhole container are polyesters (including PLA, PGA, esters of lactic acid, glycolic acid, other hydroxyacids, and copolymers thereof; polyamides and copolymers thereof; polyethers and copolymers thereof); polyurethanes, etc.

Nonlimiting examples of degradable materials that may be used include certain polymer materials that are capable of generating acids upon degradation. These polymer materials may herein be referred to as “polymeric acid precursors”; they can be used as destructible shell materials or as degradable diverting materials, depending on their properties. These materials are typically solids at room temperature. The polymeric acid precursor materials include the polymers and oligomers that hydrolyze or degrade in certain chemical environments under known and controllable conditions of temperature, time and pH to release organic acid molecules that may be referred to as “monomeric organic acids.” As used herein, the expression “monomeric organic acid” or “monomeric acid” may also include dimeric acid or acid with a small number of linked monomer units that function similarly to monomer acids composed of only one monomer unit, in that they are fully in solution at room temperature.

Polymer materials may include those polyesters obtained by polymerization of hydroxycarboxylic acids, such as the aliphatic polyesters of lactic acid, referred to as polylactic acid; of glycolic acid, referred to as polyglycolic acid; of 3-hydroxybutyric acid, referred to as polyhydroxybutyrate; of 2-hydroxyvaleric acid, referred to as polyhydroxyvalerate; of epsilon caprolactone, referred to as polyepsilon caprolactone or polycaprolactone; the polyesters obtained by esterification of hydroxyl aminoacids such as serine, threonine and tyrosine; and the copolymers obtained by mixtures of the monomers listed above. A general structure for the above-described homopolyesters is:



where R1, R2, R3, and R4 are either H, linear alkyl, such as CH₃, CH₂CH₃ (CH₂)_nCH₃, branched alkyl, aryl, alkylaryl, a functional alkyl group (bearing carboxylic acid groups, amino groups, hydroxyl groups, thiol groups, or others) or a functional aryl group (bearing carboxylic acid groups, amino groups, hydroxyl groups, thiol groups, or others);

x is an integer between 1 and 11;

y is an integer between 0 and 10; and

z is an integer between 2 and 50,000.

Under appropriate conditions (pH, temperature, water content) polyesters such as those described here may hydrolyze and degrade to yield hydroxycarboxylic acids and compounds such as those acids referred to in the foregoing as “monomeric acids.”

One example of a suitable degradable polymeric acid precursor, as mentioned above, is the polymer of lactic acid, sometimes called polylactic acid, “PLA,” polylactate or polylactide. Lactic acid is a chiral molecule and has two optical isomers. These are D-lactic acid and L-lactic acid. The poly(L-lactic acid) and poly(D-lactic acid) forms are generally crystalline in nature. Polymerization of a mixture of the L- and D-lactic acids to poly(DL-lactic acid) results in a polymer that is more amorphous in nature. The polymers described herein are essentially linear. The degree of polymerization of the linear polylactic acid can vary from as few units as necessary to make them solids under downhole conditions to several thousand units (*e.g.* 2000-5000). Cyclic structures may also be used. The degree of polymerization of these cyclic structures may be smaller than that of the linear polymers. These cyclic structures may include cyclic dimers if they are solids under storage and wellsite ambient conditions.

Another example is the polymer of glycolic acid (hydroxyacetic acid), also known as polyglycolic acid (“PGA”), or polyglycolide. Other materials suitable as polymeric acid precursors (destructible shell materials or degradable diverting materials, depending on their properties) are all those polymers of glycolic acid with itself or with other hydroxy-acid-containing moieties, for example as described in U.S. Patent Nos. 4,848,467; 4,957,165; and 4,986,355.

The polylactic acid and polyglycolic acid may each be used as homopolymers, which may contain less than about 0.1% by weight of other comonomers. As used

with reference to polylactic acid, “homopolymer(s)” is meant to include polymers of D-lactic acid, L-lactic acid and/or mixtures or copolymers of pure D-lactic acid and pure L-lactic acid. Additionally, random copolymers of lactic acid and glycolic acid and block copolymers of polylactic acid and polyglycolic acid may be used. Combinations of the described homopolymers and/or the above-described copolymers may also be used.

Other examples of polyesters of hydroxycarboxylic acids that may be used as polymeric acid precursors are the polymers of hydroxyvaleric acid (polyhydroxyvalerate), hydroxybutyric acid (polyhydroxybutyrate) and their copolymers with other hydroxycarboxylic acids. Polyesters resulting from the ring opening polymerization of lactones such as epsilon caprolactone (polyepsiloncaprolactone) or copolymers of hydroxyacids and lactones may also be used as polymeric acid precursors.

Polyesters obtained by esterification of other hydroxyl-containing acid-containing monomers such as hydroxyaminoacids may be used as polymeric acid precursors. Naturally occurring aminoacids are L-aminoacids. The three most common aminoacids that contain hydroxyl groups are L-serine, L-threonine, and L-tyrosine. These aminoacids may be polymerized to yield polyesters at the appropriate temperature and using appropriate catalysts by reaction of their alcohol and their carboxylic acid groups. D-aminoacids are less common in nature, but their polymers and copolymers may also be used as polymeric acid precursors (destructible shell or degradable diverting materials, depending upon properties). NatureWorks, LLC, Minnetonka, MN, USA, produces solid cyclic lactic acid dimer called “lactide” and from it produces lactic acid polymers, or polylactates, with varying molecular weights and degrees of crystallinity, under the generic trade name NATUREWORKS™ PLA. The PLA's currently available from NatureWorks, LLC have number average molecular weights (M_n) of up to about 100,000 and weight averaged molecular weights (M_w) of up to about 200,000, although any polylactide (made by any process by any manufacturer) may be used. Those available from NatureWorks, LLC typically have crystalline melt temperatures of from about 120 to about 170 °C, but others are obtainable. Poly(d,l-lactide) of various molecular weights is also commercially available from Bio-Invigor, Beijing and Taiwan. Bio-Invigor also

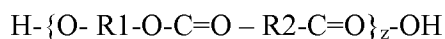
supplies polyglycolic acid (also known as polyglycolide) and various copolymers of lactic acid and glycolic acid, often called “polygalactin” or poly(lactide-co-glycolide).

The extent of the crystallinity can be controlled by the manufacturing method for homopolymers and by the manufacturing method and the ratio and distribution of lactide and glycolide for the copolymers. Additionally, the chirality of the lactic acid used also affects the crystallinity of the polymer. Polyglycolide can be made in a porous form. Some of the polymers dissolve very slowly in water before they hydrolyze.

Amorphous polymers may be useful in certain applications. An example of a commercially available amorphous polymer is that available as NATUREWORKS 4060D PLA, available from NatureWorks, LLC, which is a poly(DL-lactic acid) and contains approximately 12% by weight of D-lactic acid and has a number average molecular weight (M_n) of approximately 98,000 g/mol and a weight average molecular weight (M_w) of approximately 186,000 g/mol.

Other polymer materials that may be useful are the polyesters obtained by polymerization of polycarboxylic acid derivatives, such as dicarboxylic acid derivatives with polyhydroxy-containing compounds, in particular dihydroxy containing compounds. Polycarboxylic acid derivatives that may be used are those of dicarboxylic acids such as oxalic acid, propanedioic acid, malonic acid, fumaric acid, maleic acid, succinic acid, glutaric acid, pentanedioic acid, adipic acid, phthalic acid, isophthalic acid, terphthalic acid, aspartic acid, or glutamic acid; polycarboxylic acid derivatives are those such as of citric acid, poly and oligo acrylic acid and methacrylic acid copolymers; other materials that may be used if they are solids, or may be used as starting materials for polymerization if they are liquids, are dicarboxylic acid anhydrides, such as, maleic anhydride, succinic anhydride, pentanedioic acid anhydride, adipic acid anhydride, phthalic acid anhydride; dicarboxylic acid halides, primarily dicarboxylic acid chlorides, such as propanedioic acyl chloride, malonyl chloride, fumaroyl chloride, maleyl chloride, succinyl chloride, glutaroyl chloride, adipoyl chloride, and phthaloyl chloride. Useful polyhydroxy containing compounds for making useful degradable polymers are those dihydroxy compounds such as ethylene glycol, propylene glycol, 1,4 butanediol, 1,5 pentanediol, 1,6 hexanediol, hydroquinone, resorcinol, bisphenols such as bisphenol acetone (bisphenol A) or

bisphenol formaldehyde (bisphenol F); and polyols such as glycerol. When both a dicarboxylic acid derivative and a dihydroxy compound are used, a linear polyester results. It is understood that when one type of dicarboxylic acid is used, and one type of dihydroxy compound is used, a linear homopolyester is obtained. When multiple types of polycarboxylic acids and/or polyhydroxy containing monomers are used, copolyesters are obtained. According to the Flory Stockmayer kinetics, the “functionality” of the polycarboxylic acid monomers (number of acid groups per monomer molecule) and the “functionality” of the polyhydroxy containing monomers (number of hydroxyl groups per monomer molecule) and their respective concentrations, determine the configuration of the polymer (linear, branched, star, slightly crosslinked or fully crosslinked). All these configurations can be hydrolyzed or “degraded” to carboxylic acid monomers, and therefore can be considered as polymeric acid precursors (solids that can be used as destructible shell components or as degradable diverting material components). As one non-limiting example, not descriptive all the possible polyester structures that can be used, but providing an indication of the general structure of the most simple cases encountered, the general structure for the linear homopolyesters useful is:



where R1 and R2 are linear alkyl, branched alkyl, aryl, and alkylaryl groups; and z is an integer between 2 and 50,000.

Other examples of suitable polymeric acid precursors are the polyesters derived from phthalic acid derivatives such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthalate (PEN), and the like.

Under the appropriate conditions (for example pH, temperature, and water content) polyesters such as those described herein can “hydrolyze” and “degrade” to yield polycarboxylic acids and polyhydroxy compounds, regardless of the original polyester synthesized from any of the polycarboxylic acid derivatives listed above. The polycarboxylic acid compounds yielded by the polymer degradation process are also considered monomeric acids.

Other examples of polymer materials that may be used are those obtained by the polymerization of sulfonic acid derivatives with polyhydroxy compounds, such as polysulphones or phosphoric acid derivatives with polyhydroxy compounds, such as

polyphosphates.

Such solid polymeric acid precursor material may be capable of undergoing an irreversible breakdown into fundamental acid products downhole. As referred to herein, the term “irreversible” will be understood to mean that the solid polymeric acid precursor material, once broken downhole, does not reconstitute downhole, e.g., the material breaks down *in situ* but does not reconstitute *in situ*. The term “break down” refers to both of the two extreme cases of hydrolytic degradation that the solid polymeric acid precursor material may undergo, e.g., bulk erosion and surface erosion, and any stage of degradation in between these two. This degradation can be a result of, *inter alia*, a chemical reaction. The rate at which the chemical reaction takes place may depend on, *inter alia*, the chemicals added, temperature and time. The breakdown of solid polymeric acid precursor materials may or may not depend, at least in part, on their structure. For instance, the presence of hydrolyzable and/or oxidizable linkages in the backbone often yields a material that will break down as described herein. The rates at which such polymers break down are dependent on factors such as, but not limited to, the type of repetitive unit, composition, sequence, length, molecular geometry, molecular weight, morphology (e.g., crystallinity, size of spherulites, and orientation), hydrophilicity, hydrophobicity, surface area, and additives. The manner in which the polymer breaks down also may be affected by the environment to which the polymer is exposed, e.g., temperature, presence of moisture, oxygen, microorganisms, enzymes, pH, and the like.

Some suitable examples of solid polymeric acid precursor materials that may be used include, but are not limited to, those described in the publication in *Advances in Polymer Science*, Vol. 157, entitled “Degradable Aliphatic Polyesters,” edited by A. C. Albertsson, pages 1-138. Examples of polyesters that may be used include homopolymers, and random, block, graft, and star- and hyper-branched aliphatic polyesters.

Another class of suitable solid polymeric materials that may be used as destructible containers and/or degradable diversion materials includes polyamides and polyimides. Such polymers may comprise hydrolyzable groups in the polymer backbone that may hydrolyze under the conditions that exist downhole. Nonlimiting examples of suitable polyamides include proteins, polyaminoacids, nylon, and

poly(ϵ -caprolactam). Another class of polymers that may be suitable for use is those polymers that may contain hydrolyzable groups, not in the polymer backbone, but as pendant groups. Hydrolysis of the pendant groups may generate a water-soluble polymer and other byproducts. A nonlimiting example of such a polymer is polyvinylacetate, which upon hydrolysis forms water-soluble polyvinylalcohol and acetate salts. Other suitable materials include polysaccharides, chitins, chitosans, orthoesters, polyanhydrides, polycarbonates, poly(orthoesters), poly(ethylene oxides), and polyphosphazenes.

The shell may be made of a material that will disintegrate into smaller pieces at downhole conditions over a time which is much longer (for example at least 100 times longer, preferably at least 5 times longer, most preferably at least 3 times longer) than the time it takes to pump the container to the release location. It should be noted that some materials that disintegrate also degrade by other mechanisms and *vice versa*. Materials that eventually disintegrate include plastics such as polylactic acid (PLA), polyamides and composite materials comprising degradable plastic and non-degradable fine solids. It should be mentioned that some degradable materials pass through a disintegration stage during the degradation process. An example is PLA, which turns into a fragile material before complete degradation.

Optionally, the shell of the destructible downhole container may also be deformable and engineered to minimize the risk of premature destruction during pumping through the surface equipment and the wellbore if desired. Optionally, the shell of the destructible downhole container may be engineered to be broken during pumping through the surface equipment and the wellbore if desired. The shell may also have perforations or holes in its surface to allow fluid, for example wellbore fluid, penetration inside the destructible container. Optionally, the holes may be in the form of check valves or one-way valves such as leaf valves or leaf burst valves. Such perforations may (a) equalize the hydraulic pressure outside and inside the container and thus minimize the risk of premature destructing of the container by hydraulic pressure, and/or (b) enable greater mobility of the material inside the container, which will assist in better release of the material, such as special solid diverting material, from the container after its destruction.

Many solid diverting materials are suitable for delivery by destructible containers for the purpose of creating a fluid-diverting plug. Suitable solid diverting agents include, but are not limited to, rock salt, wax beads, oil-soluble resins, benzoic acid flakes, degradable polymer particles and fibers, cellophane flakes, various precipitates, nuts, and shells. Diversion may be used to enable treatment redirection in matrix stimulation operations below fracture pressure as well as in single or multi-stage hydraulic fracturing. In matrix stimulation the effect may be achieved by reducing the permeability of the formation because of solids penetration. The mechanism for solid-assisted diversion during fracturing operations is more complicated and is based on bridging of the fibers and/or particulates in the fracture with subsequent accumulation of additional solid material on the bridge, creating a plug. The advantage of diversion with solids over other treatment redirection methods is in lower cost and simplicity. However the amount of solid material required for effective diversion also needs to be designed properly, which is not always technically practicable, especially in multi-stage fracturing treatments. Introduction of the diverting material in a volume less than required may lead to poorer or no diversion; introduction of excess diverting material may result in its accumulation in the wellbore and possibly in a screen-out.

Diverting materials inside destructible downhole containers may be in many forms, such as particulates, approximately spherical particles, particles having aspect ratios less than about 5 and preferably less than about 3; fibers, flakes, viscous or viscosifiable fluids, and mixtures thereof. Such diverting materials may be degradable, removable, soluble in wellbore or formation fluids, or meltable. In the case of mixtures of diverting materials, some components of such mixtures may be stable at downhole conditions and some may be degradable, removable, soluble in wellbore or formation fluids, or meltable. Diverting materials may also disintegrate into smaller pieces under downhole conditions after creating seals.

In one embodiment, one example of special solid diverting materials, destructible downhole containers are filled with blends of particles designed for sealing narrow voids such as perforations, fractures, wormholes, etc. There are many such designs. In an example disclosed in U. S. Patent Application Publication No. 2009/0025934, the diverting agent is a blend including a first amount of particulates

having a first average particle size between about 2 mm and 2 cm and a second amount of particulates having a second average size between about two and ten times smaller than the first average particle size or a second amount of flakes having a second average size up to ten times smaller than the first average particle size. In another example, the blend includes a first amount of particulates having a first average particle size between about 50 to 100 % of the perforation diameter and a second amount of particulates having a second average size between about 1.6 and 20 times smaller than the first average particle size, or a second amount of flakes having a second average size up to ten times smaller than the first average particle size. Yet another example is disclosed in U. S. Patent No. 7,784,541: a blend having an amount of particles having a first average particle size between about 200 and about 2000 microns, an amount of particles having a second average particle size between about three and about ten times smaller than the first average particle size, and an amount of particles having a third average particle size smaller than the second average particle size. Yet another example is disclosed in U. S. Patent No. 7,004,255: a blend of coarse particles having diameters from about 0.20 mm to about 2.35 mm, and a quantity of smaller particles selected from medium particles, fine particles, and mixtures thereof; preferably the coarse particles have diameters from about 0.20 mm to about 0.43 mm, the medium particles have diameters from about 0.10 mm to about 0.20 mm, and the fine particles have diameters less than about 0.10 mm. In yet another example, disclosed in U. S. Patent Application Publication No. 2010/0152070, the diverting material includes a mixture of coarse particles, for example having an average particle size of from 300 to 1200 μm , medium particles, for example having an average particle size of from 20 to 150 μm and optionally fine particles, for example having an average particle size of from 5 to 15 μm , and a blend of long fibers, for example having an average length of from 8 to 15 mm and short fibers, for example having an average length of from 1 to 8 mm; the long fibers are rigid and the short fibers are flexible; the long fibers form a tridimensional mat or net, for example in a lost-circulation pathway, that traps the mixture of particles and short flexible fibers to form a plug. Yet another example is disclosed in U. S. Patent Application Publication No. 2010/0298175: a blend of coarse, medium and optional fine particles, and a blend of two different rigid fibers that includes fibers of different lengths or different diameters or different compositions, in which at least a portion of

the medium particles or coarse particles or both swells in the presence of oil. Additional blends that may be used as special solid diverting materials are known or may be developed. It is particularly important that such blends of special solid diverting materials be delivered to the diverting site with as little dilution or size or shape separation as possible; this is achieved by the destructible containers.

For enabling better release of the diverting material from the container after its destruction, the diverting material may optionally be placed inside the container in slurried form. In a slurry, there is less chance for solid/solid contacts to form and to resist mixing forces when the solids are subsequently exposed to the fluid outside the shell. The liquid phase acts as a lubricant, as well as a suspension agent, and helps the particles to be released rather than forming agglomerates that don't break apart. In one specific embodiment, diverting material is loaded into a destructible container in a dry form and then becomes slurred in wellbore fluid which penetrates the container after exposure of the container to the wellbore fluid.

The thickness of the container shell may range from about 0.01 mm to about 5 mm, preferably from about 0.05 mm to about 2 mm, and most preferably from about 0.1 mm to about 1 mm. Optionally, the container may be made with several layers, for example up to about 10 layers, that may be the same or different. Multiple layers increases the mechanical stability of the container and/or allows control of the dissolution time of the shell. In one embodiment, the material, for example special solid diverting material, is placed into heat shrinkable plastic film (for example a polyvinyl alcohol film or fabric, embossed polyvinyl alcohol film, polyethylene film, other polyolefin films, PVC film, oriented films having at least one or two oriented layers, multilayer oriented films, shrinkable polyester films such as those made of polylactic acid, polyglycolic acids or other polyesters or copolymers thereof, polysaccharide films such as starch films or cellulose films, etc.), sealed in, heated to cause shrinkage to form a container, and if desired for greater strength the first container is placed into a second heat shrinkable film, sealed in, and heated to cause shrinkage to form a stronger container. Additional films may also be used. The films may be the same or different. Such film or films may optionally be selected to degrade at a desired rate. In another embodiment the material, for example special solid diverting material, is placed into a hollow plastic ball that is initially in at least

two components that are then sealed together. In one specific example these components are two half spheres. Optionally, the components may be made of a gelatin, for example from a mixture including water, a water-soluble polymer gelatin material that may include, for example, agar or processed seaweed, non toxic white glue, and the like, plasticizers, and a preserving additive such as benzoic acid, that is formed and dried.

The tensile strength of the container shell, especially for mechanically destructible containers, is preferably in the range of from about 1 MPa to about 1000 MPa, more preferably from about 5 MPa to about 300 MPa, and most preferably from about 10 MPa to about 100 MPa. The Young's Modulus for the container shells is preferably in the range of from about 0.01 GPa to about 200 GPa, more preferably from about 0.1 GPa to about 100 GPa, and most preferably from about 0.1 GPa to about 10 GPa. For containers that dissolve, melt, react, disintegrate, etc., optionally in addition to mechanical destruction, during pumping or downhole, the preferred time for this to occur is from about 1 second to about 1 hour, more preferably from about 10 seconds to about 30 minutes, and most preferably from about 1 minute to about 15 minutes, at a preferred temperature range of from about 1 °C to about 100 °C, more preferably from about 10 °C to about 50 °C, and most preferably from about 10 °C to about 30 °C.

It is preferable to use destructible containers (with their contents) having a density similar to that of the injected fluid, although higher density destructible containers may be used at high pumping rates. The preferred density is from about 0.5 to about 5 times the fluid density, more preferably from about 1 to about 2.5 times the fluid density. The preferred density is from about 0.5 kg/L to about 5 kg/L, more preferably from about 1 kg/L to about 2.5 kg/L.

One method of manufacturing a water soluble skin containing another material is described in WO1992/022355 which discloses making a water-soluble golf ball “comprising a core, said core, formed of a first water soluble material, and an external skin formed from two skin halves or semi-spheres, said skin formed of a second water soluble material, when the two skin halves or semi-spheres and core are adhered together with a water soluble non toxic adhesive...” The skin is made for example

from paper pulp or from material selected from gelatin, agar, processed seaweed, and non toxic glue.

Containers comprising various filling materials can be made by placing such materials into hollow objects or chambers, preferably of spherical shape. Methods of making hollow plastic spheres are disclosed in Japanese Patents 56021836, 57066920, and 61239936; and Japanese Patent Application 2005349678 also discloses a plastic ball containing a closed cell foam.

U. S. Patent No. 7,395,646 discloses an article packaging device and a method for packing individual articles in a tubular thermoplastic sheet. U. S. Patent No. 7,306,093 describes a method and apparatus of packing materials, including fiber-comprising bulk materials, into a sealed package shaped like a bale. U. S. Patent No. 7,739,857 also discloses a method and apparatus for vacuum packing of fiber and other materials into one or more bales and packages. All these methods and devices may be adapted for use in some embodiments.

Containers with various fillers can also be prepared for use by surrounding portions of the fillers with a polymer or thermoplastic material. In some specific examples, shrinkable films or stretch films can be used. Shrinkable films and methods of making such films are disclosed in U. S. Patent Nos. 7,846,517 (polylactic acids), 6,340,532 (polyesters), 7,638,203 (polyesters), 7,744,806 (polyamides), and 6,340,532 (polyethylenes). A method of shrink-wrapping a material into a shrinkable plastic film with sample holes is disclosed in U. S. Patent No. 7,172,065

.A process of preparing water-soluble containers is disclosed in U. S. Patent No. 6,898,921. The process comprises a) thermoforming a first poly(vinyl alcohol) film having a water content of less than 5% to produce a pocket; b) filling the pocket with a composition; c) placing a second film on the top of the pocket; and d) sealing the first film and the second film together. The process may be adapted for use in some embodiments.

There are also disclosures of methods of making paint balls which comprise deformable mechanically destructible shells and liquidized filling compositions (for example U. S. Patent Nos. 5,254,379; 5,393,054; and 5,639,526). There are also

numerous disclosed methods of making golf balls, making multilayer golf balls, and finishing golf balls (for example U. S. Patent Nos. 5,122,046 and 6,887,135; G. B. Patent No. 2319481, and U. S. Patent Application No. 2004/092,335). These methods may be adapted to manufacture the containers filled with solids, liquids, or gases.

Destructible containers are intended to be introduced into a wellbore and pumped down to a target zone. For introducing such containers into the fluid for destruction in the wellbore, a standard or modified flow injector, for example those used for ball sealers may be placed in the high pressure line. Such devices are typically used for injection of large destructible containers (greater than about 10 mm in diameter) and the injector is commonly installed after the pumping units so the destructible containers are not subjected to forces that would break them in the surface equipment. A schematic is shown in Figure 4. Destructible containers are loaded into the accumulator, which is isolated from the main pumping line by two remotely operated valves. (Note that the same technique can be used to increase the concentration of destructible containers in the accumulator as is used to increase the concentration of particles in a fluid: use a mixture of a first size of destructible containers, and a second size of from about 7 to about 10 times smaller than the first, optionally a third size of from about 7 to about 10 times smaller than the second, and optionally additional sizes. This mixture of sizes can also be used for selective destruction (for example of selected amounts) at specific locations (for example by different-sized restrictions) and for selective delivery of different materials (in different sized destructible containers) at different locations.) Then the accumulator is closed, valves are opened and the containers are flushed from the accumulator by pumping fluid. A simple flow-through injection apparatus may also be used. When it is desired that the containers be destroyed at the surface, flow-through blenders or blenders equipped with dry additive systems can be used.

For some applications, such as treatment diversion, destructible downhole containers may be used for setting temporary seals (plugs) formed by the contents of the containers. There are several methods that may be used, if desired, for removal of the seals formed:

- *Self degradation.* Some examples of degradable materials are polyesters, including esters of lactic acid, glycolic acid, other hydroxy acids and copolymers

thereof; polyamides and copolymers thereof; polyethers and copolymers thereof; polyurethanes, etc. Other examples of degradable materials were described above.

- *Reaction with chemical agents.* Some examples of materials that may be removed by reacting with other agents are carbonates including calcium and magnesium carbonates and mixtures thereof (reactive to acids and chelating agents); acid soluble cement (reactive to acids); polyesters including PGA, PLA, esters of lactic acid, glycolic acid, other hydroxy acids, and copolymers thereof (can be hydrolyzed with acids and bases); active metals such as magnesium, aluminum, zinc and their alloys (reactive to water, acids and bases), etc.

- *Melting of at least one component of a sealing blend.* When the seal contains a meltable component, its melting results in reduction of the mechanical stability of the plug. Examples of materials that melt under downhole conditions include hydrocarbons having 30 or more carbon atoms; polycaprolactones; paraffins and waxes; carboxylic acids such as benzoic acid and its derivatives; etc.

- *Dissolution of at least one component of the sealing composition.* Plug removal is also achieved through physical dissolution of at least one of the components of the diverting blend in the surrounding fluid. Solubility of the component(s) may depend significantly on the temperature. In this case, post-treatment temperature recovery in the sealed zone can trigger the removal of the seal. Materials that dissolve in water include water-soluble polymers, water-soluble elastomers, carbonic acids, rock salt, amines, and inorganic salts. Materials that dissolve in oil include oil-soluble polymers, oil-soluble resins, oil-soluble elastomers, polyethylenes, carbonic acids, amines, and waxes.

Disintegration of at least one component of the sealing composition. Plug removal is also achieved through disintegration of the seal into smaller pieces that are flushed away. Materials that can disintegrate include plastics such as PLA, polyamides and composite materials comprising degradable plastics and non-degradable fine solids. It should be noted that some degradable materials pass through a disintegration stage during the degradation process; an example is PLA, which turns into fragile materials before complete degradation.

Although the discussion above emphasizes delivery of materials in containers that are deliberately mechanically destroyed in the wellbore, when the contents of the container comprise special solid diverting materials designed to divert fluid flow, such as fibers, fiber flocks, and other shapes designed to form plugs such as flakes, ribbons, platelets, rods, solid precipitates, grains, and pellets; mixtures of different sizes of approximately spherical materials; and mixtures of fibers and/or or other shapes such as flakes and one or more sizes of approximately spherical materials, then the container may also be destroyed by self-degradation, chemical degradation, osmotic rupturing, dissolution, melting and other mechanisms known for release of conventionally encapsulated materials delivered to a downhole location; optionally the container may be partially degraded by one of these mechanisms and then the release of the contents completed by a mechanical method. A container for special solid diverting materials may optionally be a coating that is engineered to degrade at a specific rate to release the enclosed material at a predetermined time, or pressure, or depth. In these cases, the container may optionally degrade before it reaches the zone to be treated, in which case it releases a concentrated aggregation of the container contents. This is a method of introducing slugs of an additive, for example fibers, flakes and/or or particle blends, without having to attempt to feed slugs at the surface.

In another embodiment, destructible containers are used for wellsite delivery of materials that may be difficult to handle, such as fibers, fiber flocks, fibrillated fibers, ribbons, platelets, flakes, etc. that may be difficult to transport to a well site and then to meter into a fluid. For example, fibers, fiber flocks, fibrillated fibers, ribbons, platelets, flakes, etc. may be tightly packed and enclosed in a destructible coating so that the size of the containers is, for example, in the range of about 1 to about 10 mm. Various mechanisms of coating destruction may be used, such as dissolution in water, mechanical destruction, reaction with chemicals, or combination thereof. In one specific embodiment, the coating is a film made of water, a soluble polymer such as polyvinyl alcohol, starch or a gelatin. Optionally, the gelatin may be made, for example, from a mixture including water, a water-soluble polymer gelatin material that may include, for example, agar or processed seaweed, non toxic white glue, and the like, plasticizers, and a preserving additive such as benzoic acid which quickly dissolves in water after introduction of the containers into a pumping fluid. Such containers, comprising packed fibers, fiber flocks, fibrillated fibers, ribbons,

platelets, flakes, etc., can be introduced into the treating fluid on-the-fly using the surface equipment traditionally used for wellsite delivery of proppants and other particulate materials. Such equipment includes, but is not limited to, flow-through blenders, dry-additive systems, ball injectors etc. Upon introduction of such containers into the treating fluid, the shell is destroyed, releasing the material, which is dispersed in the treating fluid. This approach has several advantages over the traditionally used methods of delivery as it enables better metering and eliminates the risk of plugging surface equipment with fibers, fiber flocks, fibrillated fibers, ribbons, flakes, etc.

Some embodiments may be understood further from the following example.

Example 1

The results of the release of particulate materials from destructible containers made by shrink-wrapping solid slurries in a 50 micron polyethylene shell are shown. The contents of the containers are shown in Table 1. The results demonstrated that the contents of the destructible container should have good fluidity to promote reliable release of the slurry into perforations upon destruction of the container.

<u>Experiment</u>	<u>Liquid Phase</u>	<u>Solid Phase</u>	<u>Total Volume</u>
1	0.5% guar solution (50% by volume)	700 μ m PLA particles (50% by volume)	65 ml
2	0.5% guar solution (40% by volume)	700 μ m PLA particles (36% by volume) 100 μ m PLA particles (15% by volume) 10 μ m PLA particles (9% by volume)	65 ml

Table 1.

It should be noted that the slurry used for filling the container in experiment 2 was designed according to the recommendations for designing high solids content fluids

given in U. S. Patent Application Publication No. 2009/0025934. Such a slurry is characterized by its high loading of solid material and good fluidity properties.

Figure 5 shows a schematic of the experimental apparatus used for studying the release of particulate materials from destructible containers. The apparatus consisted of a 50 mm transparent pipe, equipped with an injector for containers, and having one 8.4 mm perforation hole. The destructible container had an approximately spherical shape with a volume of 60 ml. The pipe was connected to a water pump having a maximum pumping capacity of 36 L/min. Before the experiment a destructible container was placed in the apparatus through the injector and the removable plug on the injector was replaced. Then the pump was started and the container was displaced to the perforation by water at the maximum pumping rate.

The following results were obtained.

- Destruction of the container in experiment 1 resulted in bridging of the particulate material at the entry of the perforation hole without squeezing of the container through the perforation.
- Destruction of the container in experiment 2 resulted in complete squeezing of the particulate matter and the shell of the container through the perforation hole.

This result demonstrated that the composition of the material in the destructible container should have good fluidity properties to enable reliable release into perforations upon destruction of the container. Example 1 shows that this approach significantly increased the reliability of delivery and release of the diverting material from a destructible container.

Claim

We claim:

1. A method of treating a downhole region penetrated by a wellbore with a treatment agent, the method comprising:
 - delivering the treatment agent to the wellsite enclosed in one or more destructible containers, each container comprising a shell;
 - inserting the one or more destructible containers into fluid being pumped down the well; and,
 - mechanically breaking the shell of the one or more destructible containers in the wellbore or in the formation to release the treatment agent.
2. The method of claim 1 wherein the one or more destructible containers comprise one or more materials.
3. The method of claim 2 wherein at least one of the materials comprising the one or more destructible containers is degradable.
4. The method of claim 1 wherein at least a portion of the treatment agent is degradable.
5. The method of claim 1 wherein breaking of the destructible container is promoted by at least partial dissolution of the shell of the container in the wellbore fluid.
6. The method of claim 1 wherein the treatment agent is in the form of a slurry inside the one or more destructible containers.
7. The method of claim 1 wherein the one or more destructible containers comprises one or more fluid flow paths allowing entry of wellbore fluid into the container.
8. The method of claim 1 wherein the wellbore is cased, the casing is perforated, and the smallest dimension of the one or more destructible containers is larger than the diameter of the perforations and the one or more destructible containers are mechanically destroyed by contact with one or more perforations.

9. The method of claim 1 wherein a restriction is placed in the wellbore to break the one or more destructible containers at a desired location, said restriction having an opening smaller than the smallest dimension of the one or more destructible containers.
10. The method of claim 1 wherein more than one restriction is placed in the wellbore, said restrictions successively smaller the farther away from the surface.
11. The method of claim 1 wherein the container breaks when a fracture or wormhole becomes smaller than the container.
12. The method of claim 1 wherein the one or more destructible containers are made by shrink wrapping one or more films around the treatment agent.
13. The method of claim 1 wherein the one or more destructible containers comprise a hollow shell into which the treatment agent is placed.
14. The method of claim 1 wherein the shell of the one or more destructible containers is made of polyvinyl alcohol or gelatin.
15. The method of claim 1 wherein a plurality of destructible containers is used and the destructible containers vary in one or more of size, composition, or contents.
16. A method of treating a downhole region penetrated by a wellbore with a special solid diverting material, the method comprising:
 - delivering the special solid diverting material to the wellsite enclosed in one or more containers, wherein each container comprises a shell;
 - inserting the one or more containers into fluid being pumped down the well; and,
 - allowing the one or more containers to release the special solid diverting material in the wellbore.
17. The method of claim 16 wherein the one or more containers comprises one or more materials.
18. The method of claim 17 wherein at least one of the materials comprising the one or more containers is at least partially degradable.

19. The method of claim 16 wherein at least a portion of the special solid diverting material is degradable.
20. The method of claim 16 wherein at least a portion of the special solid diverting material comprises a blend of particles having at least three distinct sizes.
21. The method of claim 20 wherein at least a portion of the special solid diverting material comprises one or more of fibers, fiber flocks, fibrillated fibers, ribbons, flakes or platelets.
22. The method of claim 16 wherein at least a portion of the special solid diverting material comprises one or more of fibers, fiber flocks, fibrillated fibers, ribbons, flakes or platelets.
23. The method of claim 16 wherein the special solid diverting material is in the form of a slurry inside the container.
24. The method of claim 16 wherein the one or more containers comprise one or more fluid flow paths allowing entry of wellbore fluid into the container.
25. The method of claim 16 wherein the release of the special solid diverting material is by mechanical destruction of the container.
26. The method of claim 16 wherein the release of the special solid diverting material is promoted by a chemical that reacts with the container.
27. The method of claim 16 wherein the release of the special solid diverting material is promoted by dissolution of the shell of the container in the wellbore fluid.
28. The method of claim 16 wherein the one or more containers are made by shrink wrapping one or more films around the special solid diverting material.
29. The method of claim 16 wherein the one or more containers comprise a hollow shell into which the special solid diverting material is placed.
30. The method of claim 16 wherein the shell of the one or more containers is made of polyvinyl alcohol or gelatin.
31. The method of claim 16 wherein a plurality of containers is used and the containers vary in one or more of size, composition, or contents.

32. A system for delivery of a special solid diverting material to a downhole location without dilution or separation of special solid diverting material components, said system comprising the special solid diverting material enclosed in one or more destructible containers.
33. The system of claim 32 wherein the one or more destructible containers comprises one or more materials.
34. The system of claim 33 wherein at least one of the materials comprising the one or more containers is degradable.
35. The system of claim 32 wherein the one or more destructible containers comprise one or more fluid flow paths.
36. The system of claim 32 wherein the special solid diverting material is in the form of a slurry inside the one or more destructible containers.
37. The system of claim 32 wherein the one or more destructible containers is mechanically destructible
38. The system of claim 32 wherein at least a portion of the special solid diverting material is degradable.
39. The system of claim 32 wherein the one or more destructible containers are made by shrink wrapping one or more films around the special solid diverting material.
40. The system of claim 312 wherein the one or more destructible containers comprise a hollow shell into which the special solid diverting material is placed.
41. The system of claim 32 wherein the one or more destructible containers comprises a shell made of polyvinyl alcohol or gelatin.
42. The system of claim 32 wherein a plurality of destructible containers is used and the destructible containers vary in one or more of size, composition, or contents.

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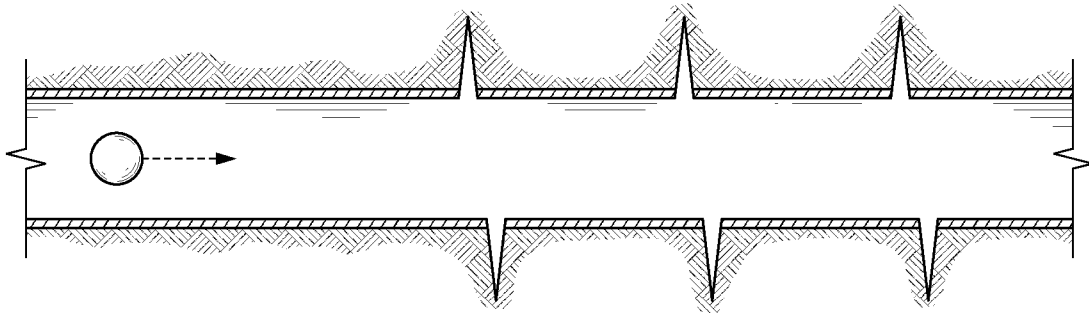


FIG. 1A

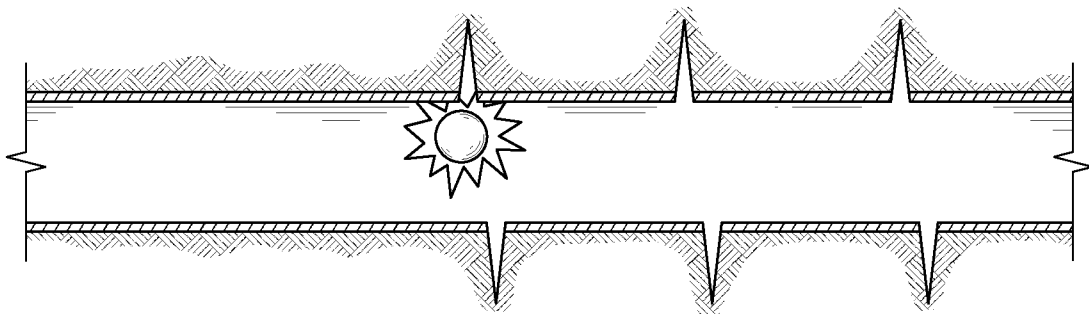


FIG. 1B

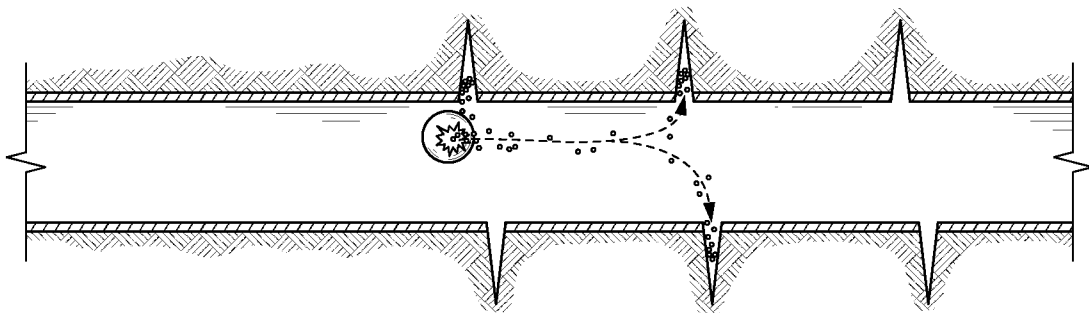


FIG. 1C

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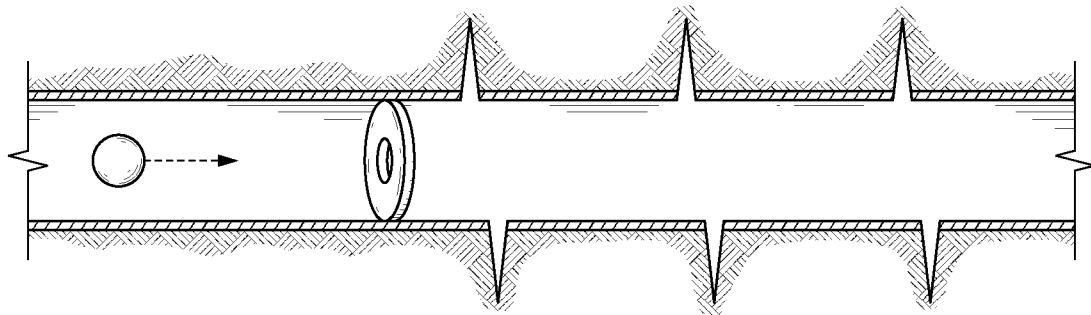


FIG. 2A

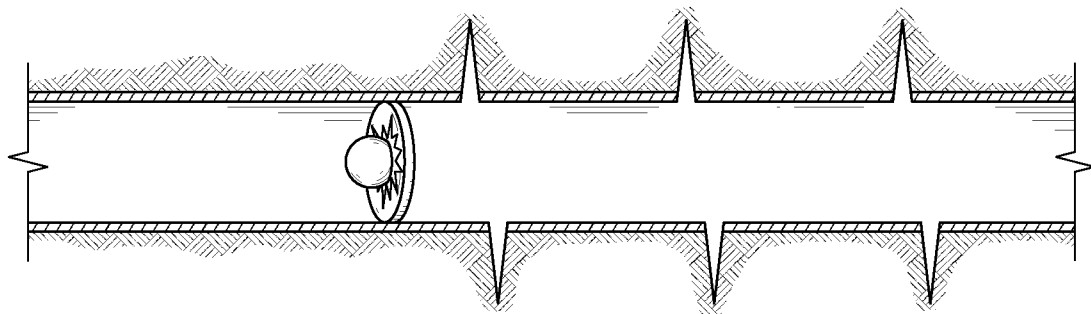


FIG. 2B

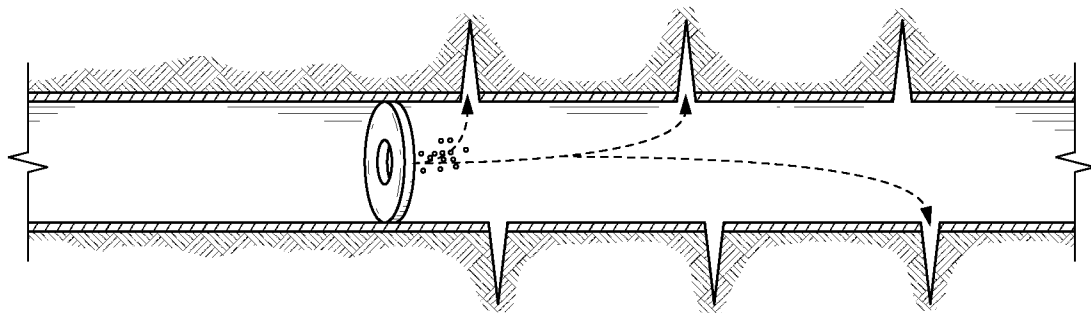


FIG. 2C

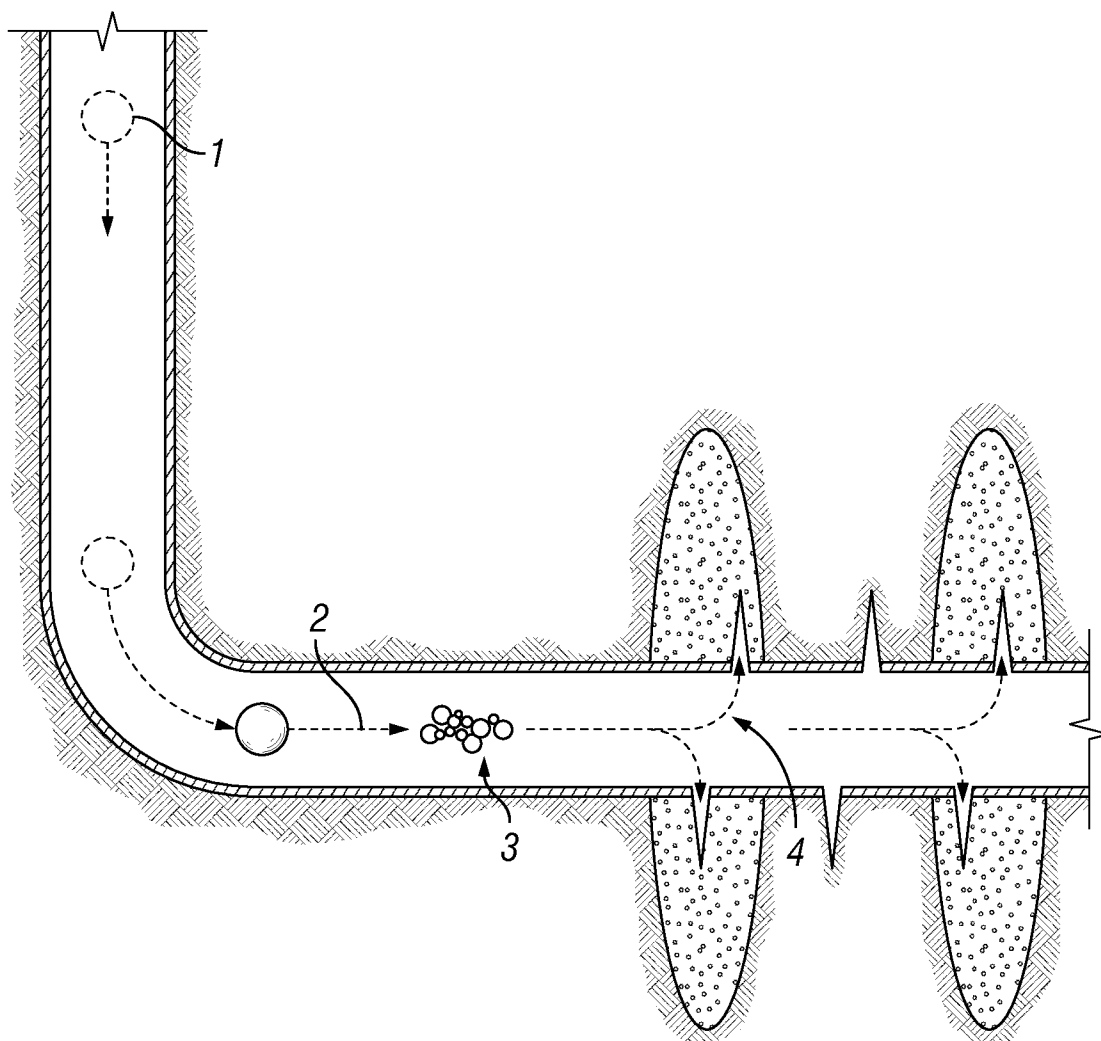


FIG. 3

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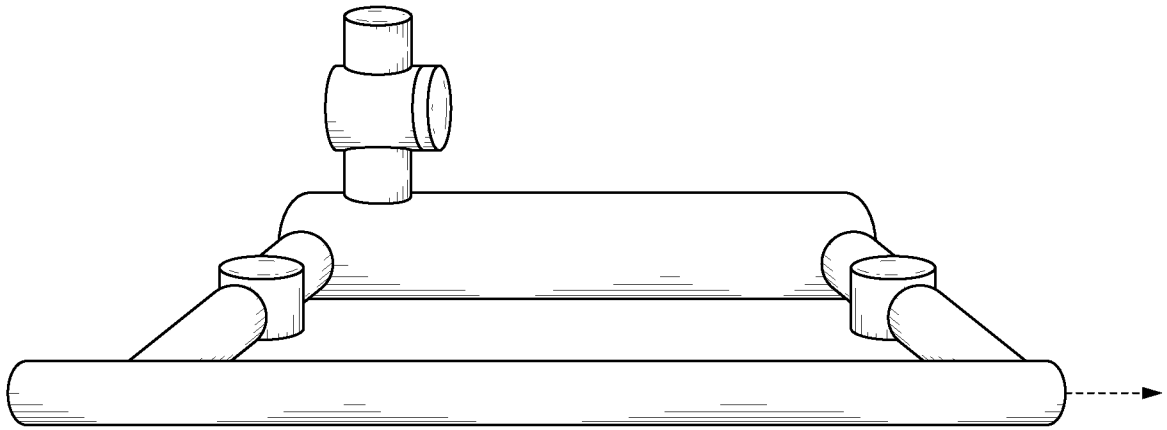


FIG. 4

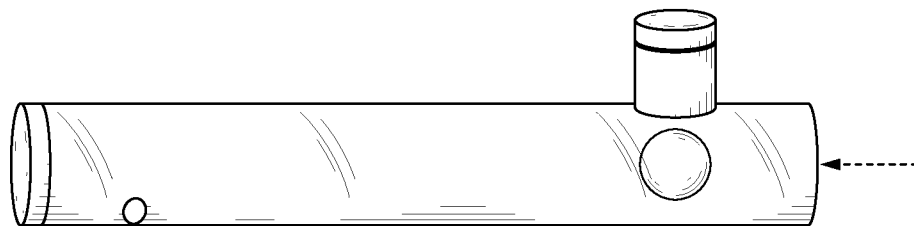


FIG. 5