



US 20120037368A1

(19) **United States**

(12) **Patent Application Publication**
EICK et al.

(10) **Pub. No.: US 2012/0037368 A1**

(43) **Pub. Date: Feb. 16, 2012**

(54) **CONTROLLED RELEASE PROPPANT**

Publication Classification

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(51) **Int. Cl.**
E21B 43/25 (2006.01)

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(52) **U.S. Cl. 166/300**

(21) Appl. No.: **13/197,879**

(57) **ABSTRACT**

(22) Filed: **Aug. 4, 2011**

Related U.S. Application Data

(60) Provisional application No. 61/373,107, filed on Aug.
12, 2010.

Materials are delivered into oil well reservoirs. Highly sensi-
tive, mechanical, biological and chemical agents can be deliv-
ered to subterranean formations with rigid, impermeable cap-
sules. A variety of treatments may be delivered to a
subterranean formation.

CONTROLLED RELEASE PROPPANT**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application is a non-provisional application which claims benefit under 35 USC §119(e) to U.S. Provisional Application Ser. No. 61/373,107 filed Aug. 12, 2010, entitled “CONTROLLED RELEASE PROPPANT,” which is incorporated herein in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] None.

FIELD OF THE DISCLOSURE

[0003] The present disclosure generally relates to the delivery of materials into oil well reservoirs.

BACKGROUND OF THE DISCLOSURE

[0004] Retrieving hydrocarbons from subterranean reservoirs is becoming more difficult as existing reserves are depleted and production becomes more expensive. It has been estimated that mature fields account for up to 70% of the world's production or more. In order to increase production, reservoirs are often treated through chemical treatments, fractures, explosions, consolidations, and other treatments that improve the recovery of hydrocarbons, both oil and gas. A variety of delivery methods have been developed to treat the formations. Coated particles, polymeric gels, and the like have been used in the past to fill in fractures and prevent water flow through. Typically formed from either a polymeric gel like acrylamide or a paraffin wax, the systems were designed to melt, diffuse, or similar process.

[0005] Fiammante, FR2548558, describes powdered products coated with a wax that melts at formation temperatures. Jacobs, U.S. Pat. No. 4,770,796, uses an encapsulated breaker for cross-linked aqueous acid-polymer gel compositions containing the same and a method for using such compositions in fracture acidizing. Manalastas, U.S. Pat. No. 5,102,558, relates to encapsulated breaker chemicals which are used in a process for forming and enlarging fractures in a subterranean formation in oil well stimulation operations. Fodge, U.S. Pat. No. 5,551,515, provide a hemicellulase that displays substantial biological activity under conditions of high temperature and high alkalinity. Ellis, U.S. Pat. No. 5,604,184, provide a resin system for coating proppants to use in hydraulic fracturing applications, for controlling the set time of resin-coated proppants in fractures, even at high temperatures, and for minimizing proppant flowback. Irwin, U.S. Pat. No. 6,225,262, provide encapsulated breakers in a slurry. Freeman, U.S. Pat. No. 6,818,594, developed active, and particularly catalytic, agents that can be made inert and remain inert under shear, temperature and prolonged exposure. Norman, U.S. Pat. No. 5,373,901 and U.S. Pat. No. 6,357,527, relates to a method for controllably breaking an aqueous based fracturing fluid utilized to stimulate a subterranean formation. Youngman, U.S. Pat. No. 6,372,678, provides preparing a spherical ceramic proppant pellet from spent fluid cracking catalyst particles. Murthy, WO2007002690, uses encapsulation and triggered-release of water-soluble or water-dispersible materials useful for controlled viscosity reduction. Rediger, US20080011477, uses thermoplastic materials as a coating on particulates (proppants). The thermoplastic coat-

ing provides the proppant with latent tackiness, such that the tackiness of the coating does not develop until the proppant is placed into the hydrocarbon-bearing formation. Barmatov, WO2009078745, provides a polymeric material for releasing a substance into a downhole fluid environment in a well. The material comprises a spherical, plastic chemical release capsule which is hard, permeable and may encapsulate a range of solids and/or liquids for subsequent release, including scale inhibitors. Pershikova, WO2009134159, teaches a sintered spherical pellet ceramic proppant, prepared from a precursor mixture that includes alumina, and a second component that is a boron source. Willberg, WO2009079231 and WO200979234, use a fluid composition comprising a multi-component article dispersed in a carrier fluid, the core having a softening point of at least 130° C.; an outer sheath that is at least one of (a) inert relative to the carrier fluid or (b) degradable under the subterranean formation conditions; and an intermediate sheath positioned between the core and the outer sheath, the intermediate sheath having a softening point up to 130° C. Heath, U.S. Pat. No. 7,196,040, provides a substance release device comprising a polymeric material for releasing a substance into a downhole fluid environment in a well. Barron, US20090288820, describe a proppant having functional features beyond serving to “prop” open fractures in a subterranean rock formation. Bicerano, US20100038083, use a composite proppant compositions comprising from approximately 0.001% to approximately 75% by volume of a coating whose electromagnetic properties change under a mechanical stress such as the closure stress of a fracture, the electromagnetic properties are detected by means of any suitable technique, to track and monitor the locations of the proppants.

[0006] Unfortunately, as oilfields become more difficult to produce, production techniques become more complex and more effective downhole delivery systems are required.

BRIEF SUMMARY OF THE DISCLOSURE

[0007] The invention more particularly provides a method of delivering highly sensitive, mechanical, biological and chemical agents to subterranean formations. In one embodiment a rigid, impermeable capsule is used to deliver a variety of treatments to a subterranean formation.

[0008] In one embodiment, materials are delivered to a subterranean reservoir by encapsulating one or more materials in a protective capsule, injecting the encapsulated material into a subterranean formation; and injecting an activator to open the encapsulated material; and activating the encapsulated material. The protective capsule forms an impermeable shell protecting the encapsulated material during delivery to the subterranean formation.

[0009] In another embodiment, materials are delivered to a subterranean reservoir by encapsulating one or more materials in a first protective capsule, encapsulating one or more materials in a second protective capsule, injecting the first and second capsules materials into a subterranean formation, and activating the encapsulated materials. The protective capsules form an impermeable shell protecting the encapsulated material during delivery to the subterranean formation.

[0010] In yet another embodiment, materials are delivered to a subterranean reservoir by encapsulating one or more materials in a first protective capsule, coating the first protective capsule with one or more materials, encapsulating the entire pellet in a second protective capsule, injecting the encapsulated materials into a subterranean formation, and

activating the encapsulated materials. At a minimum, the second protective capsule forms an impermeable shell protecting the encapsulated material during delivery to the subterranean formation.

[0011] The encapsulated material can be one or more micro-machines, biological materials, explosives, foams, adhesives, chemo-active materials and the like. The protective capsule may be made with one or more hard waxes, polypropylenes, polyethylenes, nylons, vinyls, Teflon, glass, plastics, thermoplastics, rubbers, varnish, paints, cellulose, lignins, starches, polymers, conductive polymers, metals, electrically active materials, and the like. The protective capsule can be one or more layers applied as a spray mist, drop coating, electrostatic coating, thin film, extrusion, and the like.

[0012] The encapsulated material can be components of a binary explosive with a fuel including aluminum, aluminum and sulfur, aluminum and iron oxide, aluminum and magnesium, aluminum and charcoal, cellulose, charcoal, charcoal and sugar, charcoal and sulfur, coal, coal and lignin, coal and starch, coal and sugar, glycerine, iron, iron and aluminum, lignin, magnesium, magnesium and sulfur, phosphorus sesquisulfide, polyvinylchloride (PVC), starch, sugar, sugar and aluminum, sugar and charcoal, sugar and magnesium, sulfur, sulfur and aluminum, sulfur and magnesium, sulfur and starch, zinc, zirconium hydride, combustible powder, fuel oil, nitromethane, nitroethane, and mixtures thereof; and an oxidizer including oxides, peroxides, nitrates, perchlorates, permanganates, chromates, dichromates, bromates, iodates, magnesium oxide (MgO_2), ammonium perchlorate, barium nitrate, barium oxide, barium peroxide, barium sulphate, copper oxide, cupric oxide, potassium bichromate, potassium chlorate, potassium nitrate, potassium perchlorate, potassium permanganate, red iron oxide, sodium nitrate, strontium nitrate, Zirconium phosphate-intercalated magnesium peroxide, calcium oxy-hydroxide [$CaO(OH)_2$], calcium peroxide [$Ca(OH)_2$], calcium carbonate ($CaCO_3$), lithium perchlorate, potassium with lithium chlorate, sodium chlorate with iron powder, barium peroxide with sodium chlorate, calcium peroxide, oxygen impregnated molecular sieves, oxygen impregnated zeolites, and the like.

[0013] The encapsulated material can be components of an adhesive with an adhesive resin including polyester, vinyl ester, urethane, polyurethane, rubber, acrylic, cyanoacrylate, epichlorohydrin, and the like; and a hardener including polyamines, bisphenol-A, triethylenetetramine (TETA), diethylenetetramine (DETA), and the like.

[0014] The encapsulated material can be a biological agent selected from the group consisting of an *Archae*, *Bacteria*, yeast, *Ascomycota*, unicellular organisms, *Escherichia*, *E. coli*, *Clostridia*, *C. acetobutylicum*, *Candida albicans*, *Saccharomyces cerevisiae*, *S. Pombe*, *C. difficile*, *C. perfringens*, *A. baumannii*, extremophile, iron-reducing bacteria, denitrifying bacteria, sulfate-reducing bacteria, *Desulfovibrio*, *Desulfobacteriaceae*, *acetobutylicum*, *methanobacteria*, *methanobacillus*, *methanococcus*, *methanosarcina*, one or more enzymes, peroxidase, cellulase, nutrients, powdered nutrients, cellulose, microcrystalline cellulose, sugars, glucose, bacteria containing an expression vector, bacteria containing a selection vector, bacteria containing an alkane resistance gene, bacteria containing an alkane degrading gene and combinations thereof.

[0015] The encapsulated material can be a micro electro mechanical system with a radio-frequency transmitter, gravi-

tometer, magnetometer, piezoelectric device, accelerometer, Peltier heating element, pH meter, thermometer, thermocouple, pressure sensor, inertial sensor, detonator, battery, a microchip with an antennae, a microchip with a battery and antennae, a microchip with a receiver and transmitter, a microchip with a receiver, transmitter and a battery, and combinations of these systems.

[0016] Two or more encapsulated materials can be injected simultaneously. For example, a detonator MEMS system may be injected with an explosive to achieve detonation in situ, a pH meter MEMS system may be injected with a biological agent to monitor pH during biodegradation, or a thermometer MEMS system may be injected with an adhesive to monitor curing temperatures.

DETAILED DESCRIPTION

[0017] Turning now to the detailed description of the preferred arrangement or arrangements of the present invention, it should be understood that the inventive features and concepts may be manifested in other arrangements and that the scope of the invention is not limited to the embodiments described or illustrated. The scope of the invention is intended only to be limited by the scope of the claims that follow.

[0018] Johnston, U.S. Pat. No. 3,958,638, provides an aqueous solution of a polymer that can be crosslinked to produce a gel that is passed through a wellbore and into the formation along with an encapsulated gelation agent in sufficient quantities to cause gelling of the polymer upon contact. Swanson, U.S. Pat. No. 4,246,124, uses gelled compositions that are stable and have gelation rates that can be controlled by the choice of phenolic compounds. Moradi-Araghi, U.S. Pat. No. 6,387,986, describes an encapsulated crosslinking agent and methods of Cramer and associates, US20100147512, use electrically active (EA) proppants, activate the EA proppants using a controlled electric source, and detect the electromagnetic (EM) signal with a surface antennae to determine the precise location of an artificially induced fracture in a subsurface reservoir.

[0019] Capsule, as defined herein, is a solid envelope that encloses a separate compartment containing the material to be delivered to the subterranean formation. The capsule may be constructed or applied by spray mist, extrusion, extrusion coating, or other method. The capsule must be sufficient to provide both physical resistance to pressure and prevent release of capsule contents until released in formation. In one embodiment, the capsule contains multiple compartments with a variety of encapsulated materials. In another embodiment the capsule contains an inner, shock absorbing material and a hard outer shell similar to a chicken's egg.

[0020] Capsule envelope comprises polypropylene, polyethylene, nylon, vinyl, Teflon, plastics, thermoplastics, rubber, varnish, paint, cellulose, lignin, starches, conductive polymers, metal, and electrically active materials. Capsule materials will vary greatly and are dependent upon the use and unique requirements for the encapsulating material encountered during delivery and in situ.

[0021] Capsule size may range from the size of a grain of sand to approximately golf ball sized, or from approximately 0.1 millimeters or about $\frac{4}{1000}$ ths inch to about 50 millimeters or approximately 2 inches in diameter. Capsules may require one or more layers to prevent early release due to shear forces, temperatures, and conditions encountered during transport, pumping, fracturing, and other processes with the encapsulated materials.

[0022] Encapsulated materials include micro-machines, biological materials, explosives, foams, adhesives, chemically active materials and the like. Micro-machines include vibrators, heaters, detonators, radio emitters, piezoelectric materials, microchips, gravimeters, accelerometers, antennae, batteries, and the like. Nuclear decay, fusion or fission may be used in situ to generate a detectable signal, pressure, heat, or combinations thereof. Additionally, nuclear activity may degrade the capsule and release the contents in a time dependent manner. In one embodiment a capsule contains a sensitive material and has a protective coating. In another embodiment one or more capsules contain at least one or more compartments, each with one half of a binary complex. In another embodiment a capsule may contain an explosive, adhesive, foaming agents, hygroscopic material, mechanical device, and the like. In another embodiment two capsules may each contain one half of a binary explosive, adhesive, foaming agent, crosslinking reagent, or other chemical reaction. In yet another embodiment, one capsule may contain two or more compartments each compartment containing a separate ingredient for a binary explosive, adhesive, foaming agent, crosslinking reagent, or other chemical reaction.

[0023] Soft wax and hard wax coatings can be created by modifying the ratio of ingredients in the coating material. Typically a wax coating contains paraffin, hydrocarbon wax, microcrystalline wax, oils, solvents, hardeners, and other modifiers that can be used to change the properties of the wax including hardness, melting point, and other qualities. Hardness is the firmness produced by cohesion of the wax as evidenced by its inflexibility or resistance to indentation, distortion, or scratching. Fatigue and resistance to cracking may also be influenced by the materials in the wax. A soft wax coating under one set of conditions, may behave as a hard wax coating for other conditions. In one embodiment a hard wax coating is created at cooler temperatures, the coating becomes pliable at higher temperatures, and even be liquefied at a higher temperature. The wax coating may be spray misted onto the material or pellet to be encapsulated then cooled to form a hard wax capsule that softens and melts at reservoir temperatures.

[0024] Explosive materials deflagrate or explode after ignition or detonation including fulminated mercury, nitroglycerine, dynamite, plastic explosives, binary explosives, and the like. The reaction of explosives and deflagrants (fuels) may be controlled by the rate of combustion, materials contained in the mixture, presence and rate of oxygen production, shape of the material, surface area of the material, pressure under which the reaction is initiated, and many other factors. Explosives detonate at supersonic speeds, creating an expansion shock wave. Deflagrants decompose at subsonic speeds providing a more controlled release of energy and heat. Decreased pressure, temperature, diffusion and other conditions may decrease the speed of reaction and cause an explosive to deflagrate. Increased pressure, temperature, and other conditions may increase the speed of reaction and cause a deflagrant to detonate.

[0025] Binary explosives comprise a separate fuel source and a separate oxidizer with optional fillers. Commonly known binary explosives include liquid oxygen/combustible powder (Oxyliquid), ammonium nitrate/fuel oil (ANFO), ammonium nitrate/nitromethane (Kinestik), ammonium nitrate/aluminum (Tannerite, U.S. Pat. No. 6,848,366), nitroethane/physical sensitizer (FIXOR) and other explosive combinations of fuel and oxidizer.

[0026] Deflagrants include gunpowder, black powder, propellants, cordite, carbon, sulphur, epoxies, rubbers, sugars, magnesium, zinc, iron, aluminum and plastics. Metals, charcoal, coal, sugar, starches, plastics, and the like may be atomized, dust, fine mesh, coarse mesh, powder, or a variety of grain sizes dependent upon the surface area required, desired properties, and materials used.

[0027] Fuels include aluminum, aluminum and sulfur, aluminum and iron oxide, aluminum and magnesium, aluminum and charcoal, cellulose, charcoal, charcoal and sugar, charcoal and sulfur, coal, coal and lignin, coal and starch, coal and sugar, glycerine, iron, iron and aluminum, lignin, magnesium, magnesium and sulfur, phosphorus sesquisulfide, polyvinylchloride (PVC), starch, sugar, sugar and aluminum, sugar and charcoal, sugar and magnesium, sulfur, sulfur and aluminum, sulfur and magnesium, sulfur and starch, zinc, zirconium hydride, and mixtures thereof. In some cases the deflagrant fuel may also be the encapsulating material providing both a hard outer shell and a fuel for reaction with oxygen.

[0028] Oxygen releasing compounds include oxides, peroxides, nitrates, perchlorates, permanganates, chromates, dichromates, bromates, iodates, and the like. Magnesium oxide (MgO_2), ammonium perchlorate, barium nitrate, barium oxide, barium peroxide, barium sulphate, copper oxide, cupric oxide, potassium bichromate, potassium chlorate, potassium nitrate, potassium perchlorate, potassium permanganate, red iron oxide, sodium nitrate, strontium nitrate, Zirconium phosphate-intercalated magnesium peroxide, calcium oxy-hydroxide [$CaO(OH)_2$], calcium peroxide [$Ca(OH)_2$], calcium carbonate ($CaCO_3$), lithium perchlorate, potassium with lithium chlorate (generates heat and oxygen), sodium chlorate with iron powder (generates heat and oxygen), barium peroxide with sodium chlorate, calcium peroxide, as well as oxygen impregnated molecular sieves, zeolites, and the like. A catalyst may be supplied with the oxygen releasing compound to increase the rate of oxygen production, promote release of the oxygen, or to drive the oxygen release reaction to completion. Proprietary oxygen releasing compounds are commercially available and include ORC® (Regenesis, San Clemente, Calif.), ORC® Advanced (Regenesis), EHC-O® (Adventus Group, Freeport, Ill.), O-Sox® (Adventus), EZ-Ox® (Geovation Engineering, P.C., Florida, N.Y.) and many others. Oxygen releasing compositions may be purchased in bulk for a variety of applications from aquaculture and bioremediation to in-flight and hospital oxygen supplies.

[0029] Multipart adhesives use a resin and a hardener or catalyst to form an adhesive material with a variety of expansion properties, hardening rates, and porosities. A variety of resin/hardener combinations are available including epoxy resins and amine hardeners. Adhesive resins include polyesters, vinyl esters, urethanes, polyurethanes, rubbers, acrylics, cyanoacrylates, epichlorohydrin, and the like. Hardeners and catalysts include polyamines, bisphenol-A, triethylenetetramine (TETA), diethylenetetramine (DETA), and the like. Silver-filled epoxies can be used as an electrical conductor, but most adhesives are typically electrical insulators. Fillers and additives may be used to modify the properties of the adhesive including flexibilizers, viscosity reducers, colorants, thickeners, accelerators, adhesion promoters, and the like including talc, silica, alumina, (Handbook of epoxy resins, Lee and Neville).

[0030] In one embodiment, biological agents which include whole cells, cellular extracts, enzymes, and other biological complexes would be delivered to the reservoir by encapsulation. Whole cells are living or sporulated biological cells that may include *Escherichia* such as *E. coli*, *Clostridia* such as *C. acetobutylicum*, yeast such as *Candida albicans* and *Saccharomyces cerevisiae*, and other unicellular and multicellular organisms. Unicellular organisms, particularly *Archae*, *Bacteria*, *Ascomycota*, including many extremophiles, iron-reducing bacteria, denitrifying bacteria, sulfate-reducing bacteria, *Desulfovibrio*, *Desulfobacteriaceae*, and the like are easily manipulated and may thrive under a variety of pressures, temperatures, and conditions experienced during delivery or in situ. Bacteria may be selected for the products produced, like *acetobutylicum*, *methanobacteria*, *methanobacillus*, *methanococcus*, *methanosarcina*, and the like. Commercially available *Archae*, *Bacteria* and *Yeast* are frequently manipulated either through genetic engineering, selection or natural life cycles to form spores, salt resistant, temperature resistant and combination strains that can be used in situ to perform a variety of functions including bioremediation or degradation of larger bitumens and tars into smaller fuel length hydrocarbons. For a complete list of *Archae*, *Bacteria*, *Eukaryotes* and other organisms useful as biological agents, the National Center for Biotechnology Information (NCBI), ETI BioInformatics, American Type Culture Collection (ATCC), and the European Bioinformatics Institute (EBI) maintain a variety of taxonomic and/or strain databases including the Taxonomy database at NCBI, the ATCC general collections and patent depository, and the World Biodiversity Database, as well as other publicly available databases.

[0031] In addition to biological materials and sensitive chemical reactions, in another embodiment micro-machines are protected with protective capsules for delivery in situ. Care is taken when encapsulating micro-machines to ensure the encapsulation process does not damage the micro-machine and materials used do not damage the micromachine. In one embodiment, a radio-frequency transmitter, gravimeter, magnetometer, piezoelectric device, accelerometer, peltier heating element, pH meter, thermometer, pressure sensor, inertial sensor, and other micro electro mechanical systems (MEMS) individually or interconnected to perform various actions in situ. Wireless transmitters are available from a variety of sources that interact directly with a variety of sensors to convert detected changes into radio signals and with very low voltage requirements. For more complex MEMS, batteries may be required, while for other systems, radio frequencies or electrical charges may be sufficient to obtain a measurement and generate a signal. In one embodiment a power source may be provided in the well bore, MEMS within the formation may be powered from the well bore power source through electrical induction. In another embodiment, the pellet itself is a micro-machine. In one embodiment a magnetic material is encased in a wax pellet, then coated with a polyethylene, Teflon, or other hard exterior. At formation temperatures, the wax melts and the magnetic core may be vibrated at various frequencies with changing electromagnetic pulses. The in situ seismic signal is then detected at the surface using standard geophones. In yet another embodiment, a micro-detonator is encapsulated in an explosive material with a hard impermeable shell. Several micro-detonators dispersed through one or more of the above

referenced explosive systems provide an ignition system that can ignite all of the explosive throughout the formation simultaneously.

[0032] In one embodiment, an encapsulated product is injected with proppant into a new fracture. In another embodiment, the capsule is injected with water during normal waterflooding procedures. Protective capsules are designed to be chemically, thermally, or electrically degraded releasing the contents of the capsule rapidly and without damage to the contents of the capsule. In one embodiment the protective capsule is ruptured by formation closure.

[0033] The following examples of certain embodiments of the invention are given. Each example is provided by way of explanation of the invention, one of many embodiments of the invention, and the following examples should not be read to limit, or define, the scope of the invention.

Example 1

In Situ Explosive Capsules

[0034] Delivering explosives to a formation can be risky. Explosives can detonate accidentally, get damaged during handling, or become disoriented during delivery. Downhole, explosives are typically delivered in the well bore and do not penetrate to a great extent into the formation. To improve explosive delivery to the formation, a binary explosive can be encapsulated within impermeable capsules that do not rupture prematurely and remain sealed until released by conditions within the formation.

[0035] In one embodiment an aluminum powder is pressed with paraffin to generate an aluminum powder pellet. The aluminum powder pellet is spray mist coated with one or more coats of a hard varnish or polyurethane encapsulating material. Aluminum nitrate is packaged separately in a polypropylene pellet. The aluminum nitrate powder pellet is coated with one or more coats of hard polypropylene or polyethylene to generate an encapsulated pellet. The aluminum powder pellet and aluminum nitrate pellet can then be mixed and handled without risk. Although not required, the two pellets may be transported separately and mixed immediately prior to delivery. During pellet manufacture the density and size of the pellets may be regulated to obtain a similar size distribution, density and transportation characteristics. The pellets are delivered with a fracture fluid that is maintained below the melting point of the varnish, polypropylene, and paraffin. After the pellets have penetrated the formation the temperature may be increased or a solvent may be delivered, allowing the aluminum and aluminum nitrate to mix deep within the formation. Application of heat, friction or electrical spark can ignite the Tannerite. A detonator within the well bore can initiate the explosion which will propagate through the formation to all of the mixed aluminum and aluminum nitrate.

[0036] In another embodiment the aluminum powder pellet is mixed with dark flake aluminium powder, Titanium powder and zirconium hydroxide. In yet another embodiment, 90% 600-mesh dark flake aluminium powder, 5% 325-mesh Titanium sponge and 5% 200-mesh zirconium hydroxide are used to create pellets that are subsequently coated with a hard, impermeable wax. Additionally, the aluminum nitrate may be a mixture of ammonium nitrate and ammonium perchlorate. In one embodiment, the aluminum nitrate pellet contains 85% 200-mesh ammonium nitrate and 15% ammonium perchlorate.

ate. Ratios of explosive and oxidizer can be optimized for formation properties including temperature, pressure, and hydrocarbons present.

[0037] In another embodiment, to ensure uniform delivery of a binary explosive system, a single pellet is manufactured that contains an exact ratio of reactant and catalyst/oxidizer. A pellet of FIXOR™ flammable liquid is cooled below freezing and coated with a hard wax. FIXOR is made up of two parts, a flammable liquid (FIXOR Liquid, U.N. 2842, NSN 1375-21-920-4587) and unreactive powder (FIXOR Powder, NSN 1375-21-920-4638). The wax pellet is coated with FIXOR™ dry powder mixed with a soft wax. The entire pellet is then coated with a hard wax or polyurethane. Once pumped into the formation, the paraffin wax will melt, dispersing the FIXOR™ powder within the liquid to create an explosive. Once detonated through electrical shock, electrical detonators, detonation cord or other detonation method, the explosion will propagate throughout the formation. Undetonated FIXOR will deactivate over time removing the risk of accidental detonation during subsequent formation treatments.

[0038] In yet another embodiment, deflagration may be used to heat the formation rapidly in a controlled manner. By delivering a flammable material and an oxygen source as described above either in individual capsules delivered simultaneously or as an interior capsule and an outer coating. The oxygen source may either be on the exterior of the dual layer pellet or on the interior with the deflagration agent on the surface. The rate of oxygen release can control the rate of phosphorous combustion thus controlling the heat of the reaction. Pelletizing polypropylene powder with sodium chlorate and iron powder creates an oxygen generating bead. Deflagrants may be corned into small spherical balls or extruded into cylinders or flakes. The properties of the deflagrant are greatly influenced by the size and shape of its grains. The surface of the grains influences the speed of burning, and the shape influences the surface and its change during burning. By selection of the grain shape it is possible to influence the pressure vs time curve as the deflagrant burns. Combining the oxygen generating bead with the extruded deflagrant in a hard wax mixture provides a sustainable burning material that can be used to increase formation temperature rapidly in a controlled manner. Ignition of the beads surrounding the bore hole will provide heat and ignition for the adjacent beads, allowing the deflagration reaction to propagate throughout the formation. Because the reaction is slowed, each bead igniting adjacent beads, the pressure can be released, maintained or allowed to increase as the reaction progresses simply by releasing or retaining pressure at the well bore.

[0039] Using a hard outer shell, or capsule, combinations of fuel and oxidizer may be delivered in separate sealed compartments and activated in situ. Activation in situ means the explosives are easier to handle and damage to the materials, moisture, and the like can be prevented until the capsules are activated and the explosives are ignited. This provides a more active composition that is protected from the environment and can be injected deep into the formation

Example 2

Expansion Adhesive

[0040] In another embodiment, a binary chemical reaction can be used to dissolve a foaming adhesive within the formation. A pellet comprising commercially available Gorilla Glue™ in a cellulose gel capsule is coated with a hard wax coating.

The pellets are mixed with the fracturing fluid. If the fracturing fluid is aqueous, it should be kept below the melting temperature of the hard wax coating. The appropriate ratio of aqueous solution and Gorilla Glue™ are then delivered to the reservoir. Under the heat of the reservoir, the wax melts, the cellulose dissolves in the aqueous solution, and the Gorilla Glue™ is released. Once released, the glue is activated in aqueous solution. Once the foaming adhesive is activated it expands to adhere sand and loosely consolidated formation or maintain fracturing to greater distances within the formation. After the adhesive is cured, the fracturing pressure may be reduced and new fractures will be maintained.

[0041] In another embodiment, a two-part structural adhesive is prepared by extruding thermoplastic pellets filled with liquid urethane. A second thermoplastic pellet is filled with liquid TETA. The thermoplastic pellets, which may be a variety of colors, are mixed to achieve a desired ratio of urethane and TETA which can vary greatly dependent upon the final properties desired. The mixed pellets are injected with a fracture fluid until the desired fracture pressure is reached. Once fracture pressure is achieved, the formation is sealed and the temperature of the thermoplastic pellets increases until the urethane and TETA are released. Upon mixing the urethane and TETA expand, generating heat and pressure causing more thermoplastic pellets to rupture while maintaining fracture pressures for an extended period. Once the urethane is set, the pressure may be released and the fractures are maintained by the foamed adhesive and incorporated thermoplastic materials.

Example 3

Biologicals

[0042] Biological materials may be packaged using care when generating the protective capsules. Once the capsules are delivered, the biological material may be released and activated in situ to achieve desired byproducts, convert the heavy oils and bitumens into lighter oils and fuels that can be more easily produced. Species like *acetobutylicum* can live in an oxygen free environment (anaerobic) and will survive in the formation dependent upon the nutrients that are available or supplied. *S. cerevisiae* may live in either an aerobic or anaerobic environment producing different products dependent upon the growth conditions. *E. coli* will undergo rapid growth with oxygen (aerobic) generating products while oxygen is present but will grow more slowly or go dormant once oxygen is depleted.

[0043] In one embodiment, *C. acetobutylicum* containing a cellulase selection vector is grown to density under anaerobic conditions with a cellulose carbon source. On the cellulase selection vector is one expression construct (promoter and open reading frame) comprising the cellulase gene and one expression construct comprising the one or more alkane response (alk) genes. Alternatively, *C. difficile*, *C. perfringens*, *A. baumannii* or other known species may be similarly prepared dependent upon the growth characteristics required in situ. One or more genes may be expressed from either native genes or expression vectors. The expression vector may be selectable, as in the cellulase/alkane construct described above, or it may be incorporated through recombination into the genome. The cells above are grown to density and sporulation is induced. The sporulated cultures are dried, powdered, and mixed with growth media before encapsulation in a cellulose shell. The hard cellulose shell is permeable

to aqueous solutions, but impervious to exterior pressures and shear forces. Thus the bacterial spores are completely protected until the cellulose pellets are exposed to an aqueous solution. Once an aqueous environment is encountered in situ, the cellulase enzyme in the bacteria degrades the hard shell, and the alkane expressing acetobutylicum can begin degrading long alkane chains in tar and bitumen formations.

[0044] In another embodiment, a mutated *Desulfobacteriaceae* is selected for temperature, pressure, and acid resistance. The selected bacteria is grown to density, pelleted, and resuspended in a 10% glycerol solution. The resuspended cells are quickly freeze dried in a lyophilizer and subsequently powdered. The powdered cells are mixed with nutrients, a powdered yeast extract or LB broth, and packed into capsules. These soft capsules are then coated in material with a protective, water resistant, outer shell, either a urethane or hard wax. The coated particles may be mixed with fracturing fluid or other delivery solution that does not appreciably dissolve the hard shell during the delivery process. The hard shell will protect the cells inside the capsule during delivery, like an egg. These materials would be delivered to the well site, once delivered to the subterranean reservoir, pressure within the reservoir is reduced and the compacting formation will apply uneven pressure to the hard shell, cracking the hard shell. This leaves the soft, water soluble capsule exposed to any aqueous solutions within the formation. The capsule dissolves and the biological agent, resistant *Desulfobacteriaceae*, is activated in situ. In one embodiment, biological agents at depth can be used to convert heavy oils to lighter agents and fuel oils. In another embodiment, *Desulfobacteriaceae* digest alkanes within tar layers producing smaller fuel grade byproducts. The field of biological agents is very broad, so these examples are merely demonstrative examples of the principals involved. They are not construed to be an exhaustive list of uses.

Example 4

Micro-Machines

[0045] Micro-mechanical devices are available in a variety of formats to achieve a variety of functions. A MEMS device may be designed for use in situ that accounts for formation conditions, delivery conditions, desired activity and other factors. In one embodiment a MEMS chip is synthesized with a wireless radio receiver/transmitter and a sensor. Once the microchip is designed and synthesized, the wafer containing one or more microchip, typically hundreds of microchips, is cut and the individual chips may be packaged. In one embodiment the chips are wrapped in a soft wax to protect the circuitry and allow the wax to be shaped without damage. Once protected by wax, a hard shell is applied to the outer wax, the hard shell may be a spray mist of urethane or the sensor may be encased in Teflon to create an impervious shell. In another embodiment the microchip is encased in Teflon while the membrane sensor is encased in a hard wax. Once in situ, the hard wax melts, exposing the sensor membrane to the formation conditions.

[0046] In one embodiment, a batch of pH sensitive sensors is synthesized where each microchip comprises a wireless receiver/transmitter, a pH sensitive membrane and a small in-board battery. Hundreds or thousands of sensors may be assembled on one or more wafers, reducing costs while increasing reproducibility. The microchip and electrical components of the sensor are protected in a rubber, polypropy-

lene, Teflon, or other plastic coating. The membrane is protected with a soft wax coating. The entire device is coated with a hard wax layer. The hard wax and soft wax having a relatively low melting point below formation temperature, yet the melting point is higher than the waterflooding solution. One or more of the sensors may be calibrated to formation conditions by placing the sensor at in waterflooding solution and increasing the temperature and pressure to that of the formation. The pH is then recorded at one or more known pH standards, the pH standards in some cases are above and below the maximum and minimum pH values to be measured in situ. One or more pH sensors may be delivered in situ to assess waterflooding conditions. After delivery of the pH sensors to the formation, the temperature of the waterflood solution may be raised above the melting point of the wax coating. Waterflooding may then progress until a desired pH is measured throughout the formation. A temporary or permanent relay may be placed in the wellbore to receive measurements from the pH sensors in the formation. The pH may be modified and monitored over a period of time as formation treatments change.

[0047] In another embodiment, a temperature sensitive sensor is designed with a thermocouple, a wireless receiver/transmitter, a small in-board battery. As described above, hundreds or thousands of microchips may be manufactured on one or more wafers. As previously stated, decreasing size increases reliability while decreasing costs. Because the thermocouple does not need to be exposed to measure temperature, the entire microchip may be encased in a Teflon or glass coating through an extrusion or deposition process. The protected thermocouple may be delivered in situ with other sensors to monitor a wide range of temperatures. The thermocouple may be encased in a durable ceramic shell that can withstand pyrolysis temperatures used in some thermal production methods like SAGD, VAPEX, in situ combustion, and the like. In some cases the entire thermocouple and wireless transmitter should be manufactured out of high temperature resistant materials. In other systems, a battery may not be used and instead the thermocouple and wireless transmitter respond passively to radio frequency transmissions.

[0048] In yet another embodiment, lead zirconate titanate crystals are electroplated with a conductive material, gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium, graphite, or the like. Optionally, a second wax coating impregnated with graphite, or other conductive material, is layered on the electroplated piezoelectric crystals. Once protected the electroplated crystals are injected into the wellbore. An electrical charge is applied with varying frequency and a signal is generated within the reservoir. Alternatively, the piezoelectric material is vibrated rapidly, generating frictional heat.

Example 5

Systems

[0049] The micro-machines, explosives, adhesives, and/or biological materials may be injected simultaneously to achieve active systems in situ. In one embodiment a micro-detonator comprising a detonation circuit and explosive as described above is injected with the components of a deflagrant and a temperature resistant thermocouple. By mixing the binary deflagrant with a small fraction of detonators and thermocouples, the explosive can be ignited and temperature

monitored simultaneously ensuring that the explosive is completely detonated and the entire formation has reached a sufficient temperature.

[0050] In closing, it should be noted that the discussion of any reference is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. At the same time, each and every claim below is hereby incorporated into this detailed description or specification as a additional embodiments of the present invention.

[0051] Although the systems and processes described herein have been described in detail, it should be understood that various changes, substitutions, and alterations can be made without departing from the spirit and scope of the invention as defined by the following claims. Those skilled in the art may be able to study the preferred embodiments and identify other ways to practice the invention that are not exactly as described herein. It is the intent of the inventors that variations and equivalents of the invention are within the scope of the claims while the description, abstract and drawings are not to be used to limit the scope of the invention. The invention is specifically intended to be as broad as the claims below and their equivalents.

REFERENCES

[0052] All of the references cited herein are expressly incorporated by reference. The discussion of any reference is not an admission that it is prior art to the present invention, especially any reference that may have a publication data after the priority date of this application. Incorporated references are listed again here for convenience:

- [0053] 1. U.S. Pat. No. 3,958,638, Phillips Petroleum Co. (Johnston), Priority: 6/75
- [0054] 2. U.S. Pat. No. 4,246,124, U.S. Pat. No. 4,323,123, and U.S. Pat. No. 4,440,228, Phillips Petroleum Co. (Swanson), Priority: 7/78
- [0055] 3. U.S. Pat. No. 4,770,796, Petrolite Corp. (Jacobs), Priority: 11/87
- [0056] 4. U.S. Pat. No. 5,102,558, U.S. Pat. No. 5,102,559, U.S. Pat. No. 5,110,486, U.S. Pat. No. 5,187,011, U.S. Pat. No. 5,192,615, U.S. Pat. No. 5,204,183, WO9212327, WO9212328, WO9217683, Exxon Res. Dev. Co. (Manalastas), Priority: 12/89
- [0057] 5. U.S. Pat. No. 5,373,901, Halliburton Energy Services (Norman), Priority: 5/00
- [0058] 6. U.S. Pat. No. 5,551,515, WO9118974, Chemgen Corp (Fodge), Priority: 5/90.
- [0059] 7. U.S. Pat. No. 5,604,184, WO9812416, Texaco (Ellis), Priority: 4/95
- [0060] 8. U.S. Pat. No. 6,225,262, U.S. Pat. No. 5,990,315, WO9963199, 3M Innovative Properties Co. (Irwin), Priority: 5/98
- [0061] 9. U.S. Pat. No. 6,357,527, Halliburton Energy Services (Norman), Priority: 5/00
- [0062] 10. U.S. Pat. No. 6,372,678, US2002058581, WO0226656, Fairmount Minerals Ltd (Youngman), Priority: 9/00
- [0063] 11. U.S. Pat. No. 6,387,986, WO0100746, Phillips Petroleum (Moradi-Araghi), Priority: 6/99
- [0064] 12. U.S. Pat. No. 6,444,316, U.S. Pat. No. 6,527,051, U.S. Pat. No. 6,554,071, Halliburton Energy Sery (Reddy), Priority: 5/00
- [0065] 13. U.S. Pat. No. 6,818,594, US2005130845, WO0134939, M-I Llc. (Freeman), Priority: 11/99

- [0066] 14. U.S. Pat. No. 6,848,366, US2003033952, Tannerite Company (Tanner), Priority: 8/01
- [0067] 15. U.S. Pat. No. 7,196,040, US2004043906, WO0194744, T R Oil Services Ltd (Heath), Priority: 6/00
- [0068] 16. US20080011477, US2008202750, WO2008008625, WO2009111697, Georgia Pacific Chem (Rediger), Priority: 7/06
- [0069] 17. US20090288820, WO2010011402, Oxane Materials Inc. (Barron) Priority: 5/08
- [0070] 18. US20100038083, WO2010019424, Sun Drilling (Bicerano) Priority: 8/08
- [0071] 19. US20100147512, WO2010068401, Conoco-Phillips Co. (Eick) Priority: 12/08
- [0072] 20. WO2007002690, Rice Univ. (Murthy), Priority: 6/05
- [0073] 21. WO2009078745, Schlumberger Tech (Barmatov), Priority: 12/07
- [0074] 22. WO2009134159, Schlumberger Tech (Per-shikova), Priority: 4/08
- [0075] 23. WO2009079231, Schlumberger Tech (Willberg), Priority: 12/07
- [0076] 24. WO2009079234, Schlumberger Tech (Willberg), Priority: 12/07
- [0077] 25. FR2548558, Petroles Cie Francaise (Fiam-mante) Priority: 7/83
- [0078] 26. Lee and Neville, "Handbook of epoxy resins,"

1. A method of delivering materials to a subterranean reservoir comprising:

- a) encapsulating a material in a protective capsule;
- b) injecting the encapsulated material into a subterranean formation;
- c) injecting an activator to open encapsulated material; and
- d) activating the encapsulated material,

wherein said protective capsule forms an impermeable shell and said encapsulated material is protected during delivery to the subterranean formation.

2. The method of claim 1, wherein said encapsulated material is selected from the group consisting of micro-machines, biological materials, explosives, foams, adhesives, chemo-active materials and combinations thereof.

3. The method of claim 1, wherein said protective capsule comprises hard wax, polypropylene, polyethylene, nylon, vinyl, Teflon, glass, plastic, thermoplastic, rubber, varnish, paint, cellulose, lignin, starch, one or more polymers, one or more conductive polymers, metal, electrically active materials, or and combinations thereof.

4. The method of claim 1, wherein said protective capsule is applied as a spray mist, drop coating, electrostatic coating, thin film, extrusion, in one or more applications.

5. The method of claim 1, wherein said encapsulated material is a component of a binary explosive comprising:

- a) a fuel selected from the group consisting of aluminum, aluminum and sulfur, aluminum and iron oxide, aluminum and magnesium, aluminum and charcoal, cellulose, charcoal, charcoal and sugar, charcoal and sulfur, coal, coal and lignin, coal and starch, coal and sugar, glycerine, iron, iron and aluminum, lignin, magnesium, magnesium and sulfur, phosphorus sesquisulfide, polyvinyl-chloride (PVC), starch, sugar, sugar and aluminum, sugar and charcoal, sugar and magnesium, sulfur, sulfur and aluminum, sulfur and magnesium, sulfur and starch, zinc, zirconium hydride, combustible powder, fuel oil, nitromethane, nitroethane, and mixtures thereof and

b) an oxidizer selected from the group consisting of oxides, peroxides, nitrates, perchlorates, permanganates, chromates, dichromates, bromates, iodates, magnesium oxide (MgO_2), ammonium perchlorate, barium nitrate, barium oxide, barium peroxide, barium sulphate, copper oxide, cupric oxide, potassium bichromate, potassium chlorate, potassium nitrate, potassium perchlorate, potassium permanganate, red iron oxide, sodium nitrate, strontium nitrate, Zirconium phosphate-intercalated magnesium peroxide, calcium oxy-hydroxide [$\text{CaO}(\text{OH})_2$], calcium peroxide [$\text{Ca}(\text{OH})_2$], calcium carbonate (CaCO_3), lithium perchlorate, potassium with lithium chlorate, sodium chlorate with iron powder, barium peroxide with sodium chlorate, calcium peroxide, oxygen impregnated molecular sieves, oxygen impregnated zeolites, and combinations thereof.

6. The method of claim 1, wherein said encapsulated material is a component of an adhesive comprising:

- a) an adhesive resin selected from the group consisting of polyester, vinylester, urethane, polyurethane, rubber, acrylic, cyanoacrylate, epichlorohydrin, and combinations thereof; and
- b) a hardener selected from the group consisting of polyamines, bisphenol-A, triethylenetetramine (TETA), diethylenetetramine (DETA), and combinations thereof.

7. The method of claim 1, wherein said encapsulated material is a biological agent selected from the group consisting of an *archae*, bacteria, yeast, *Ascomycota*, unicellular organisms, *Escherichia*, *E. coli*, *Clostridia*, *C. acetobutylicum*, *Candida albicans*, *Saccharomyces cerevisiae*, *S. Pombe*, *C. difficile*, *C. perfringens*, *A. baumannii*, extremophile, iron-reducing bacteria, denitrifying bacteria, sulfate-reducing bacteria, *Desulfovibrio*, *Desulfobacteriaceae*, *acetobutylicum*, *methanobacteria*, *methanobacillus*, *methanococcus*, *methanosarcina*, one or more enzymes, peroxidase, cellulase, nutrients, powdered nutrients, cellulose, microcrystalline cellulose, sugars, glucose, bacteria containing an expression vector, bacteria containing a selection vector, bacteria containing an alkane resistance gene, bacteria containing an alkane degrading gene and combinations thereof.

8. The method of claim 1, wherein said encapsulated material is a micro electro mechanical system comprising one or more components selected from the group consisting of a radio-frequency transmitter; gravitometer; magnetometer; piezoelectric device; accelerometer; Peltier heating element; pH meter; thermometer; thermocouple; pressure sensor; inertial sensor; detonator; battery; a microchip with an antennae; a microchip with a battery and antennae; a microchip with a receiver and transmitter; a microchip with a receiver, transmitter and a battery; and combinations thereof.

9. The method of claim 1, wherein two or more encapsulated materials are injected simultaneously.

10. A method of delivering materials to a subterranean reservoir comprising:

- a) encapsulating a first material in a first protective capsule;
- b) encapsulating a second material in a second protective capsule;
- c) injecting the first and second encapsulated materials into a subterranean formation; and
- d) activating the encapsulated materials;

wherein said first and second protective capsules form an impermeable shell and said encapsulated materials are protected during delivery to the subterranean formation.

11. The method of claim 10, wherein said encapsulated material is selected from the group consisting of micro-machines, biological materials, explosives, foams, adhesives, chemo-active materials and combinations thereof.

12. The method of claim 10, wherein said protective capsule comprises hard wax, polypropylene, polyethylene, nylon, vinyl, Teflon, glass, plastic, thermoplastic, rubber, varnish, paint, cellulose, lignin, starch, one or more polymers, one or more conductive polymers, metal, electrically active materials, or and combinations thereof.

13. The method of claim 10, wherein said protective capsule is applied as a spray mist, drop coating, electrostatic coating, thin film, extrusion, in one or more applications.

14. The method of claim 10, wherein said encapsulated material is a component of a binary explosive comprising:

- a) a fuel selected from the group consisting of aluminum, aluminum and sulfur, aluminum and iron oxide, aluminum and magnesium, aluminum and charcoal, cellulose, charcoal, charcoal and sugar, charcoal and sulfur, coal, coal and lignin, coal and starch, coal and sugar, glycerine, iron, iron and aluminum, lignin, magnesium, magnesium and sulfur, phosphorus sesquisulfide, polyvinylchloride (PVC), starch, sugar, sugar and aluminum, sugar and charcoal, sugar and magnesium, sulfur, sulfur and aluminum, sulfur and magnesium, sulfur and starch, zinc, zirconium hydride, combustible powder, fuel oil, nitromethane, nitroethane, and mixtures thereof; and

- b) an oxidizer selected from the group consisting of oxides, peroxides, nitrates, perchlorates, permanganates, chromates, dichromates, bromates, iodates, magnesium oxide (MgO_2), ammonium perchlorate, barium nitrate, barium oxide, barium peroxide, barium sulphate, copper oxide, cupric oxide, potassium bichromate, potassium chlorate, potassium nitrate, potassium perchlorate, potassium permanganate, red iron oxide, sodium nitrate, strontium nitrate, Zirconium phosphate-intercalated magnesium peroxide, calcium oxy-hydroxide [$\text{CaO}(\text{OH})_2$], calcium peroxide [$\text{Ca}(\text{OH})_2$], calcium carbonate (CaCO_3), lithium perchlorate, potassium with lithium chlorate, sodium chlorate with iron powder, barium peroxide with sodium chlorate, calcium peroxide, oxygen impregnated molecular sieves, oxygen impregnated zeolites, and combinations thereof.

15. The method of claim 10, wherein said encapsulated material is a component of an adhesive comprising:

- a) an adhesive resin selected from the group consisting of polyester, vinylester, urethane, polyurethane, rubber, acrylic, cyanoacrylate, epichlorohydrin, and combinations thereof; and
- b) a hardener selected from the group consisting of polyamines, bisphenol-A, triethylenetetramine (TETA), diethylenetetramine (DETA), and combinations thereof.

16. The method of claim 10, wherein said encapsulated material is a biological agent selected from the group consisting of an *archae*, bacteria, yeast, *Ascomycota*, unicellular organisms, *Escherichia*, *E. coli*, *Clostridia*, *C. acetobutylicum*, *Candida albicans*, *Saccharomyces cerevisiae*, *S. Pombe*, *C. difficile*, *C. perfringens*, *A. baumannii*, extremophile, iron-reducing bacteria, denitrifying bacteria, sulfate-reducing bacteria, *Desulfovibrio*, *Desulfobacteriaceae*, *acetobutylicum*, *methanobacteria*, *methanobacillus*, *methanococcus*, *methanosarcina*, one or more enzymes, peroxidase, cellulase, nutrients, powdered nutrients, cellulose, microcrystalline cellulose, sugars, glucose, bacteria containing an expression

vector, bacteria containing a selection vector, bacteria containing an alkane resistance gene, bacteria containing an alkane degrading gene and combinations thereof.

17. The method of claim 10, wherein said encapsulated material is a micro electro mechanical system comprising one or more components selected from the group consisting of a radio-frequency transmitter; gravitometer; magnetometer; piezoelectric device; accelerometer; Peltier heating element; pH meter; thermometer; thermocouple; pressure sensor; inertial sensor; detonator; battery; a microchip with an antennae; a microchip with a battery and antennae; a microchip with a receiver and transmitter; a microchip with a receiver, transmitter and a battery; and combinations thereof.

18. The method of claim 10, wherein two or more encapsulated materials are injected simultaneously.

19. A method of delivering materials to a subterranean reservoir comprising:

- a) encapsulating a first material in a first protective capsule;
- b) coating the first capsule with a second material;
- c) encapsulating the entire pellet in a second protective capsule;
- d) injecting the encapsulated materials into a subterranean formation; and
- e) activating the encapsulated materials,

wherein said first and second protective capsules form an impermeable shell and said encapsulated materials are protected during delivery to the subterranean formation.

20. The method of claim 19, wherein said encapsulated material is selected from the group consisting of micro-machines, biological materials, explosives, foams, adhesives, chemo-active materials and combinations thereof.

21. The method of claim 19, wherein said protective capsule comprises hard wax, polypropylene, polyethylene, nylon, vinyl, Teflon, glass, plastic, thermoplastic, rubber, varnish, paint, cellulose, lignin, starch, one or more polymers, one or more conductive polymers, metal, electrically active materials, or and combinations thereof.

22. The method of claim 19, wherein said protective capsule is applied as a spray mist, drop coating, electrostatic coating, thin film, extrusion, in one or more applications.

23. The method of claim 19, wherein said encapsulated material is a component of a binary explosive comprising:

- a) a fuel selected from the group consisting of aluminum, aluminum and sulfur, aluminum and iron oxide, aluminum and magnesium, aluminum and charcoal, cellulose, charcoal, charcoal and sugar, charcoal and sulfur, coal, coal and lignin, coal and starch, coal and sugar, glycerine, iron, iron and aluminum, lignin, magnesium, magnesium and sulfur, phosphorus sesquisulfide, polyvinylchloride (PVC), starch, sugar, sugar and aluminum, sugar and charcoal, sugar and magnesium, sulfur, sulfur and aluminum, sulfur and magnesium, sulfur and starch, zinc, zirconium hydride, combustible powder, fuel oil, nitromethane, nitroethane, and mixtures thereof and

- b) an oxidizer selected from the group consisting of oxides, peroxides, nitrates, perchlorates, permanganates, chromates, dichromates, bromates, iodates, magnesium oxide (MgO_2), ammonium perchlorate, barium nitrate, barium oxide, barium peroxide, barium sulphate, copper oxide, cupric oxide, potassium bichromate, potassium chlorate, potassium nitrate, potassium perchlorate, potassium permanganate, red iron oxide, sodium nitrate, strontium nitrate, Zirconium phosphate-intercalated magnesium peroxide, calcium oxy-hydroxide [$CaO(OH)_2$], calcium peroxide [$Ca(OH)_2$], calcium carbonate ($CaCO_3$), lithium perchlorate, potassium with lithium chlorate, sodium chlorate with iron powder, barium peroxide with sodium chlorate, calcium peroxide, oxygen impregnated molecular sieves, oxygen impregnated zeolites, and combinations thereof.

24. The method of claim 19, wherein said encapsulated material is a component of an adhesive comprising:

- a) an adhesive resin selected from the group consisting of polyester, vinylester, urethane, polyurethane, rubber, acrylic, cyanoacrylate, epichlorohydrin, and combinations thereof and
- b) a hardener selected from the group consisting of polyamines, bisphenol-A, triethylenetetramine (TETA), diethylenetetramine (DETA), and combinations thereof.

25. The method of claim 19, wherein said encapsulated material is a biological agent selected from the group consisting of an *archae*, bacteria, yeast, *Ascomycota*, unicellular organisms, *Escherichia*, *E. coli*, *Clostridia*, *C. acetobutylicum*, *Candida albicans*, *Saccharomyces cerevisiae*, *S. Pombe*, *C. difficile*, *C. perfringens*, *A. baumannii*, extremophile, iron-reducing bacteria, denitrifying bacteria, sulfate-reducing bacteria, *Desulfovibrio*, *Desulfobacteriaceae*, *acetobutylicum*, *methanobacteria*, *methanobaccilus*, *methanococcus*, *methanosarcina*, one or more enzymes, peroxidase, cellulase, nutrients, powdered nutrients, cellulose, microcrystalline cellulose, sugars, glucose, bacteria containing an expression vector, bacteria containing a selection vector, bacteria containing an alkane resistance gene, bacteria containing an alkane degrading gene and combinations thereof.

26. The method of claim 19, wherein said encapsulated material is a micro electro mechanical system comprising one or more components selected from the group consisting of a radio-frequency transmitter; gravitometer; magnetometer; piezoelectric device; accelerometer; Peltier heating element; pH meter; thermometer; thermocouple; pressure sensor; inertial sensor; detonator; battery; a microchip with an antennae; a microchip with a battery and antennae; a microchip with a receiver and transmitter; a microchip with a receiver, transmitter and a battery; and combinations thereof.

27. The method of claim 19, wherein two or more encapsulated materials are injected simultaneously.

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