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(54) Title: FLUID LOSS CONTROL AGENT

(57) Abstract: A composition for treating a hydrocarbon-bearing subterranean formation penetrated by a wellbore which composition comprises a wellbore fluid having dispersed therein a fluid loss control agent comprising a first solid phase comprising a first solid material and a second solid phase comprising a second solid material wherein the melting points of the first and the second solid materials are above the temperature of the near wellbore region of the formation and the first and second solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the temperature of the near wellbore region of the formation.



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FLUID LOSS CONTROL AGENT

The present invention relates to a composition and method for temporarily reducing the permeability of subterranean formations and, in particular, relates to a composition and method for controlling fluid injection and chemical placement into subterranean formations during well treatments.

5 At various times during the life of a well, formed in a subterranean formation for the production of oil or gas, it is desirable to treat the well. Such treatments include perforating, gravel packing, fracturing, acidizing and inhibiting scale deposition. These treatments generally involve filling the wellbore with a standing or circulating treating fluid or the injection of a treating fluid into the formation. Although high fluid

10 permeability is an important characteristic of a hydrocarbon-producing formation, these treatments may be adversely affected by the uncontrolled loss of treating fluid into the highly permeable formations. For example, in an acidizing treatment where it is desired to treat the least permeable formation strata to improve its permeability, the formation strata having the higher permeability will most likely consume the major portion of the

15 treatment fluid leaving the least permeable formation strata virtually untreated. Similarly, during treatments to inhibit scale deposition, it is desirable to introduce a scale inhibitor into formation strata which are producing scaling water. Where hydrocarbon-bearing strata of the formation have a higher permeability or lower formation pressure than such water-producing strata, the major proportion of the

20 treatment fluid will most likely enter the hydrocarbon-bearing strata leaving the water-producing strata virtually untreated. Therefore, it is desirable to control the injectivity of treating fluids to the high permeability (or low pressure) formation strata during such

treatments. During fracturing treatments, it is desirable to control loss of the treating fluid to the formation to allow propagation of the fracture. During perforating operations, it is desirable to prevent fluids from entering the formation and damaging the formation. During gravel pack operations, it is desirable to recover the expensive workover fluids from the wellbore after completion of the operation. Therefore, the efficient performance of some treatments of the wellbore require temporarily reducing the permeability of formation strata so as to reduce the loss of treating fluid or to control the injection of treating fluid into these formation strata during treatment. Several fluid loss control agents have been developed for use in these treatments.

One type of prior fluid loss control agent comprises finely divided solids dispersed in the treating fluid. As the treating fluid leaks off into the formation, the finely divided solid materials are filtered out onto the face of the formation and form a filter cake. The filter cake functions to restrict the flow of fluid therethrough and substantially reduces treatment fluid leak off to the formation. Prior types of solid materials include crushed naphthalene and benzoic acid, crushed oyster shells, silica flower or guar-coated silica flower or crushed limestone and rock salt. The water-soluble materials dissolve during the treatment operation and therefore are unsuitable in many cases. The inert materials form a solid filter cake which remains on the formation face after completion of the treatment thereby causing, in some cases, permanent damage to the production capability of the formation.

Other types of fluid loss control agents comprise oil-soluble, water-insoluble materials. Prior art materials include soaps, gels, waxes, and various types of polymers or resins such as those disclosed in SPE Papers 5662 (1975) and 5713 (1976) and U.S. Pat. Nos. 3,998,272; 3,979,304; 3,979,305; 3,989,632; 3,882,029; 3,181,612; 3,252,904, 3,336,979 and 3,319,716 which discloses oil soluble polyesters. These materials are mixed with the treatment fluid and are injected into the wellbore. These materials also form a filter cake on the face of the formation to prevent treatment fluid leakoff. It was intended that these materials be dissolved in the subterranean hydrocarbon fluids as the temperature of the formation increases after the treatment operation. Although these materials were suitable in some applications, in fracturing treatments and treatment of gas wells, these materials, in some cases, left a residue on the face of the formation after completion of the treatment thereby causing permanent damage to the production

capabilities of the formation.

Water soluble and acid degradable polymeric fluid loss control agents have also been utilized in the prior art as disclosed in U.S. Pat. No. 3,319,716 and SPE Papers 3653 (1971). A field practice of removing these materials after treatment involves
5 acidizing the formation after treatment. Although these materials were suitable in some applications, in those cases where there was incomplete acid contact with the fluid loss control material, these materials also left a residue in the formation after treatment thereby damaging the production capabilities of the well.

Another type of fluid loss control agent known as ball sealers has been
10 developed for use during diversion treatments in cased perforated wellbores. The diversion treatments generally comprise diverting the treating fluid from the more permeable formation strata to the least permeable formation strata to enable treatment of the least permeable formation strata. The ball sealers, which generally comprise small, rubber-coated balls, are suspended in the treating fluid and pumped into the well along
15 with the treating fluid. The balls are carried down the interior of the casing to the perforations communicating with the high permeability formation strata. The ball sealers seat on these perforations and divert the treating fluid to formation strata having lower permeability. In some applications, the presence of the ball sealers in the wellbore after the treatment present operational problems.

20 Accordingly, there is still a need for a fluid loss control agent which can effectively control fluid placement during treatment operations and is capable of being removed from the well after treatment operations without leaving any residue in the wellbore or on the formation strata.

The present invention relates to a composition and method for controlling the
25 injection of a treatment fluid into a hydrocarbon-bearing subterranean formation penetrated by a wellbore.

Thus, according to a first embodiment of the present invention there is provided a composition for treating a hydrocarbon-bearing subterranean formation penetrated by a wellbore which composition comprises a wellbore fluid having dispersed therein a
30 fluid loss control agent comprising a first solid phase comprising a first solid material and a second solid phase comprising a second solid material wherein the melting points of the first solid material and the second solid material are above the temperature of the

near wellbore region of the formation and the first solid material and the second solid material are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the temperature of the near wellbore region of the formation.

5 By "near wellbore region of the formation" is meant a radial distance of less than 100 feet, preferably less than 50 feet, more preferably, less than 30 feet from the well bore.

When the composition of the present invention is injected into a wellbore, it is envisaged that the eutectic combination may be formed through diffusion of the first
10 solid material from the first solid phase into the second solid phase and/or the diffusion of the second solid material from the second solid phase into the first solid phase (hereinafter referred to as "inter-diffusion").

The liquid phase mixture of the eutectic combination may be in equilibrium with the first solid material and/or the second solid material. Alternatively, the eutectic
15 combination may consist solely of a liquid phase mixture of the first and second materials.

Suitably, the eutectic combination has a eutectic temperature at or below the temperature in the near wellbore region of the formation. The eutectic temperature for two solid materials is defined herein as the lowest temperature at which a liquid phase
20 mixture of the two materials can exist in equilibrium with either or both of the two solid materials.

Preferably, the mole ratio of the first and second solid materials in the composition of the present invention is at or close to the eutectic composition for a mixture of the first and second materials which is defined herein as the composition at
25 the eutectic temperature.

Optionally, the fluid loss control agent may comprise at least one further solid phase comprising a further solid material, for example, 3 to 4 further solid phases comprising a third and fourth solid material respectively. Thus, the eutectic combination is preferably a binary, ternary or quaternary combination formed from two,
30 three or four solid materials respectively.

The solid materials that may be combined to form the eutectic combination include acetaminophen, N-acetylcarbazole, acetylsalicylic acid, p-aminophenol,

benzamide, 1,4-benzenediol (hydroquinone), benzil, benzo-(c)-cinnoline, benzoic acid, camphor, carbazole, p-dichlorobenzene, 2,2-dimethoxy-1,2-diphenylethanone, N,N-diphenylacetamide, diphenylamine, ethyl-p-aminobenzoate, glutaric acid, 2-hydroxybenzoic acid, (4-methoxyphenyl)diazene-1-oxide, naphthalene, naphthylamine, m-nitroaniline, phenanthrene, phenanthridine, phenyl salicylate, poly(oxyethylene) and propyphenazone. Preferred eutectic combinations include: acetaminophen and at least one of p-aminophenol and propyphenazone; phenanthrene and at least one of benzo-(c)-cinnoline and phenanthridine; benzoic acid and at least one of salicylic acid, acetylsalicylic acid, ethyl-p-aminobenzoate, benzamide, ethyl p-aminobenzoate and n-butyl p-hydroxybenzoate; phenacetin and at least one of benzamide and p-aminobenzoic acid; camphor and at least one of hydroquinone and naphthalene; naphthalene and at least one of p-dichlorobenzene and diphenylamine; poly(oxyethylene) and at least one of glutaric acid, benzoic acid and 1,2-diphenylethane; and benzamide and p-chlorobenzoic acid. A particularly suitable eutectic combination is hydroquinone and camphor. Suitably, the mole % of hydroquinone in the composition of the present invention is in the range 20 to 80 mole %, preferably, 25 to 55 mole %, more preferably 28 to 40 mole % based on the total amount of hydroquinone and camphor.

Suitably, the wellbore fluid is an aqueous fluid or an organic fluid. Suitably, the water used to form the aqueous wellbore fluid may be pure water, tap water, deionised water, seawater, sulphate reduced seawater, aquifer water or a synthetic brine. Suitably, the organic wellbore fluid may be xylene, toluene, diesel, methanol, glycol, glycol ethers, biodiesel, kerosene, base oil, or oil produced by the well being treated. It is also envisaged that the wellbore fluid may be a water-in-oil emulsion or an oil-in-water emulsion.

In a first aspect of the present invention, the wellbore fluid has dispersed therein pellets comprising at least one discrete region of the first solid phase and at least one discrete region of the second solid phase. Optionally, the pellets may comprise at least one discrete region of a further solid phase comprising a further solid material. The pellets may range in size from finely divided solids to larger structures such as ball sealers. The pellets may be in the form of particles that are sized such that they are capable of entering perforation tunnels formed in the casing and cement of a cased wellbore. For certain treatments, the particles are sized such that they do not enter and

bridge the pore throats of the formation. Where the particles are sized such that they do not enter the formation, the particles preferably have an average diameter greater than 25 microns, more preferably in the range 25 to 500 microns, most preferably 50 to 250 microns. For other treatments, the particles are finely divided and may therefore enter
5 the formation. It is envisaged that the finely divided particles that enter the formation may form a filter cake in the near wellbore region of the formation. Suitably, such finely divided particles have a diameter of 100% less than 10 microns, preferably 100% less than 5 microns, for example, 100% less than 2 microns. The pellets may also be in the form of ball sealers having an average diameter of, for example, from 1 to 2.5 cm
10 depending on the size of the perforations in the casing.

The pellets of this first aspect of the present invention may comprise a compressed mixture of first particles comprising the first solid material and second particles comprising the second solid material. Optionally, the compressed pellets may comprise further particles comprising a further solid material. Thus, the first, second
15 and optional further particles comprise the first, second and optional further solid phases respectively of the fluid loss control agent. Suitably, the particles which are compressed to form the pellets have a diameter of less than 150 microns, preferably less than 75 microns, more preferably less than 25 microns, for example, less than 10 microns. Suitably, the particles may be formed by separately comminuting the first solid material,
20 the second solid material and the optional further solid material to form fine powders. Preferably, where the first, second or optional further solid material is malleable at ambient temperature, the material is comminuted at a temperature below the freezing point of the solid material, for example, via freeze fracturing or cold grinding. The powders are then well mixed and pellitised. The pellets may be formed by pressing the
25 mixed powders in a mould. Alternatively, the mixed powders may be extruded under pressure through a die followed by chopping the extrudate into small cylinders. Preferably, the cylinders are converted into substantially spherical pellets in a spheronizer. Preferably, the resulting pellets have an average diameter greater than 25 microns, more preferably in the range 25 to 500 microns, most preferably 50 to 250
30 microns. The resulting pellets may also be in the form of ball sealers having an average diameter of, for example, from 1 to 2.5cm depending on the size of the perforation in the casing.

The pellets of this first aspect of the present invention may comprise a core of the first solid phase and a shell or coating layer of the second solid phase (hereinafter “core and shell pellets”). Suitably, the coating layer has a thickness of 2 to 50% of the diameter of the core. Preferably, the thickness of the coating layer is selected such that the mole ratio of the first solid material to the second solid material is at or close to the eutectic composition. Where the first solid material of the core is soluble in the wellbore fluid, it is preferred that the second solid material of the shell or coating layer is substantially insoluble therein. Optionally, the pellets may comprise at least one further coating layer of a further solid phase, preferably one further coating layer of a further solid phase. It is also envisaged that larger pellets, for example, ball sealers, may comprise further concentrically arranged layers of the first solid phase, second solid phase and optional further solid phase.

Suitably, the core and shell pellets may be prepared in a continuous fluidised bed wherein dry pellets of the first solid material (hereinafter “core pellets”) are mechanically fluidised and sprayed with an atomised solution of the second solid material dissolved in a volatile solvent so that a shell or coating layer of the second solid material gradually builds up on the core pellets. Alternatively, the core and shell pellets may be formed using a spinning coating disc wherein the second solid material is melted and the core pellets are suspended in the melt of the second solid material (hereinafter referred to as “molten coating material”) and the resulting suspension is passed over a rotating disc under conditions giving, at the edge of the disc, a liquid film of excess molten coating material between liquid coated core pellets where the thickness of the liquid film is substantially less than the diameter of the liquid coated core pellets. As the liquid film of excess molten coating material leaves the disc, the film is atomized into liquid droplets having a mean diameter substantially less than the mean diameter of the liquid coated core pellets. The atomized liquid droplets and liquid coated core pellets pass from the disc into a tower at or near the top thereof. The molten liquid solidifies as the liquid coated core pellets and the atomized droplets fall through the tower thereby generating core and shell pellets and particles of excess coating material respectively. The particles of excess coating material are then separated from the core and shell pellets using conventional separation techniques. The particles of excess coating material are then melted and recycled to the spinning coating disc. The core and

shell pellets may also be formed using the technique of pan coating wherein dry core pellets are placed in a horizontally positioned perforated pan. At least one pneumatically actuated atomising nozzle is positioned directly above the pan and the coating material (either molten or in solution) is sprayed from the nozzle(s) onto the core pellets so that a shell or coating layer gradually builds up on the core pellets. The air used to drive the nozzle(s) also serves to dry the core and shell pellets. The drying rate may be adjusted by regulating the air flow to the nozzle(s). The core and shell pellets may also be formed using the technique of granulation wherein a solution or suspension of the coating is sprayed onto the core pellets in a granulator, for example, a fluidized bed granulator. Suitable fluidized bed granulators are manufactured by Glatt (Germany) or Aeromatic (Switzerland). Optionally, the resulting core and shell pellets may be coated with a further solid phase comprising a further solid material using any of the above techniques.

Where the core and shell pellets are in the form of particles having a size of less than 150 microns, preferably less than 75 microns, more preferably less than 25 microns, for example, less than 10 microns, these particles may be compressed into larger structures, as described above. Preferably, the larger structures are substantially spherical particles having an average diameter of greater than 25 microns, more preferably in the range 25 to 500 microns, most preferably in the range 50 to 250 microns. The larger structures may also be ball sealers having an average diameter of, for example 1 to 2.5 cm depending on the size of the perforations in the casing.

The pellets of this first aspect of the present invention may also comprise a continuous first solid phase comprising the first solid material and a discontinuous second solid phase comprising the second solid material. Optionally, a discontinuous further solid phase comprising a further solid material is dispersed in the continuous first solid phase. Preferably, the continuous first solid phase is substantially insoluble in the wellbore fluid. Suitably, the discontinuous second solid phase comprises finely divided particles of the second solid material that are dispersed in the continuous first solid phase. Suitably, the discontinuous further solid phase comprises finely divided particles of the further solid material dispersed in the continuous first solid phase. Suitably, the finely divided particles that are dispersed in the first solid phase have a size of less than 150 microns, preferably less than 75 microns, more preferably less than

25 microns, for example, less than 10 microns. The finely divided particles may be formed by comminution of the second solid material and optionally the further solid material, as described above. Suitably, the second solid material and the optional further solid material have a melting point substantially above that of the first solid material. Accordingly, the pellets may be formed by dispersing the finely divided particles in the first solid phase at a temperature above the melting point of the first solid material but below the melting point of the second solid material and the optional further solid material, extruding the resulting mixture through a die into a cooling bath, and pelletizing the extrudate, as described above. The resulting pellets may be in the form of substantially spherical particles having an average diameter of greater than 25 microns, more preferably in the range 25 to 500 microns, most preferably 50 to 250 microns. The pellets may be also in the form of larger structures such as ball sealers having an average diameter of, for example, from 1 to 2.5 cm depending on the size of the perforations in the casing.

In a second aspect of the present invention, the wellbore fluid has dispersed therein first pellets comprising the first solid phase and second pellets comprising the second solid phase. Accordingly, inter-diffusion of the first and second solid materials will not occur until after the composition has been injected down a wellbore and the first and second pellets have intimately mixed, for example, when a filter cake of the first and second pellets has accumulated in the near wellbore region of the formation and/or against the rock face of the wellbore or when the first and second pellets have accumulated in a perforation of a cased wellbore. This has an advantage of avoiding premature degradation of the pellets during storage. Optionally, the wellbore also has dispersed therein further pellets comprising a further solid phase.

The first pellets, second pellets and optional further pellets of this second aspect of the present invention may range in size from finely divided particles to distinct solid structures. Preferably, the distinct solid structures are substantially spherical. Preferably, the first, second and optional further pellets are in the form of particles. Suitably, the particles may be sized such that they are capable of entering perforation tunnels formed in the casing and cement of a cased wellbore. For certain treatments, the particles are sized such that they do not enter and bridge the pore throats of the formation. Where the particles are sized such that they do not enter the formation, the

particles preferably have an average diameter greater than 25 microns, more preferably in the range 25 to 500 microns, most preferably 50 to 250 microns. For other treatments, finely divided first, second and optional further particles may enter the formation and form a filter cake in the near wellbore region of the formation. Suitably, such finely divided first, second and optional further particles have a diameter of 100% less than 10 microns, preferably 100% less than 5 microns, for example, 100% less than 2 microns.

The first, second and optional further pellets may be formed by separately comminuting the first, second and optional further solid materials respectively to the desired size. However, it is also envisaged that finely divided first particles comprising the first solid material, finely divided second particles comprising the second solid material and optionally, finely divided further particles comprising the further solid material may be compressed into first, second and optional further pellets respectively of the desired size. Suitably, the finely divided particles which are compressed to form the first, second and optional further pellets have a diameter of less than 150 microns, preferably less than 75 microns, more preferably less than 25 microns, for example, less than 10 microns. Suitably, the finely divided particles are prepared by separately comminuting the first, second and optional further solid materials to form fine powders, as described above. The pellets are then formed by separately pressing the powders in moulds or by separately extruding the powders under pressure through a die, as described above. It is also envisaged that the first, second and optional further pellets may be formed by separately softening the first, second and optional further solid materials and then separately extruding the softened materials through a die into a cooling bath, and pelletizing the extrudates, for example, by chopping the extrudate into small cylinders. Suitably, the resulting pellets may be converted into substantially spherical pellets in a spheronizer. The pellets preferably have an average diameter of greater than 25 microns, more preferably in the range 25 to 500 microns, most preferably in the range 50 to 250 microns.

The pellets of the fluid loss control agent of the first and second aspects of the present invention are preferably substantially insoluble in the wellbore fluid. However, it is envisaged that where the pellets are soluble in the wellbore fluid, the pellets may be coated with a polymer which disperses in water or oil above a threshold temperature,

preferably, at or above the temperature at which the eutectic combination is formed. Suitably, prior to its dissipation, the coating of polymer reduces the rate of diffusion of wellbore fluid into the pellets. Where the fluid loss control agent is formed by compressing finely divided particles into pellets, the individual particles employed to form the pellets may be coated with the polymer.

Suitably, the polymer used for coating the finely divided particles and/or pellets may be a water-soluble polymer or an oil-soluble polymer. Preferred water-soluble polymers for coating the particles and/or pellets include polyacrylic acids; polymaleic acids; polyacrylamide; polymethacrylate; polyvinylsulphonates; copolymers of monomers selected from the group consisting of acrylic acid, maleic acid, acrylamide, methacrylate, 2-acrylamido-2-methylpropane-sulfonic acid, and vinylsulphonate; lignosulphonates; hydroxy methyl cellulose; carboxy methyl cellulose; carboxy methyl ethyl cellulose; hydroxy methyl ethyl cellulose; hydroxyl propyl methyl cellulose; methyl hydroxy propyl cellulose; sodium alginates; polyvinyl pyrrolidone; polyvinyl pyrrolidone acrylic acid co-polymers; polyvinyl pyrrolidone caprolactam co-polymers; polyvinyl alcohol; polyphosphates, polystyrene-maleinates, poloxamers and poloxamines. Suitably, the poloxamers are linear ABA block co-polymers having the general structure $(EO)_n-(PO)_m-(EO)_n$ where n and m are integers and EO and PO represents structural units derived from ethylene oxide and propylene oxide respectively. Suitably, the poloxamines are ABA block co-polymers having a branched structure with a central ethylene diamine bridge i.e. $[(EO)_n-(PO)_m]_2-N-CH_2-CH_2-N-[(EO)_n-(PO)_m]_2$ where n , m , EO and PO have the same meaning as for the poloxamers. Preferably, the water-soluble polymer has a molecular weight in the range 1,000-100,000, preferably 5,000 to 30,000, for example, 15,000 to 25,000. Preferred oil-soluble polymers for coating the particles and/or pellets include polyethers, polyamine derivatives or carbon backbone polymers having pendant nitrogen and/or oxygen atoms as described in EP 0902859 which is herein incorporated by reference.

In a further embodiment of the present invention there is provided a method of reducing the permeability of a hydrocarbon-bearing subterranean formation penetrated by a wellbore which comprises introducing the composition of the present invention into a wellbore.

The wellbore fluid of the composition may be a carrier fluid or a treating fluid.

The wellbore fluid may be injected into the wellbore and into the formation. Alternatively, the wellbore may be filled with a standing or circulating wellbore fluid. Preferably, the first, second and optional further solid phases of the fluid loss control agent may be suspended in a first slug of the wellbore fluid which is pumped into the wellbore during treatment. The first slug of wellbore fluid may be a portion of a treating fluid or a carrier fluid preceding the treatment fluid. As this first slug of wellbore fluid flows into the more permeable formation strata, the first, second and optional further solid phases of the fluid loss control agent reduce the permeability of these formation strata thereby diverting the second slug of fluid to less permeable formation strata. Alternatively, the wellbore fluid may be used to equalize the permeability of all the formation strata and enable injection of equal volumes of treating fluid to all the strata. It is also envisaged that the first, second and optional further solid phases of the fluid loss control agent may be added continuously into the treating fluid or may be suspended in a plurality of slugs of a carrier fluid. Thus, alternate slugs of the fluid loss control agent in the carrier fluid and of the treating fluid may be injected into the wellbore. In fracturing treatments, the fluid loss control agent is normally dispersed in the fracturing fluid and minimizes fluid loss during the treatment to maintain the wedging effect and propagate the fracture. In other applications, such as perforating or gravel packing, a high concentration slug of the fluid loss agent dispersed in the wellbore fluid may be placed at the appropriate location of the wellbore during the treatment.

Preferably, the composition that is injected into the wellbore comprises pellets of the fluid loss agent dispersed in the wellbore fluid. The pellets of the fluid loss control agent should substantially maintain their integrity during the well treatment but should be capable of degrading after completion of the well treatment. This is achieved through inter-diffusion of the first, second and optional further solid materials resulting in the formation of an eutectic combination comprising a liquid phase mixture of the first, second and optional further solid materials which is subsequently carried out of the wellbore with the formation fluids after the wellbore is put back on production.

Where the composition employed in the method of the present invention comprises a wellbore fluid having dispersed therein pellets comprising at least one discrete region of the first solid phase, at least one discrete region of the second solid

phase, and optionally at least one discrete region of a further solid phase, it is preferred that the eutectic temperature of the eutectic combination is substantially above the ambient surface temperature such that there is no discernable degradation of the pellets during storage prior to their injection into the wellbore. This will allow the pellets to be
5 stored at the well site without special precautions until their use. Preferably, the eutectic temperature of the eutectic combination is at least 40°C, preferably at least 50°C.

However, without wishing to be bound by any theory, the rate of inter-diffusion of the first, second and optional further solid materials at the ambient surface temperature will be substantially less than the rate of inter-diffusion at the temperature of the near
10 wellbore region of the formation. Accordingly, where the eutectic combination comprises a liquid phase mixture of the first, second and optional further materials at ambient temperature, the pellets may be stored for short periods of up to several days without significant degradation of the pellets.

The amount of pellets of the fluid loss control material required to enable
15 successful fluid loss control will vary widely depending upon the size of the formation, the degree of permeability of the formation, the size of the pellets and other variables, such as wellbore fluid viscosity and permissible fluid loss volumes

After the composition has been injected into the wellbore, the fluid loss control agent either acts to minimize penetration of the treating fluid into the formation or to
20 divert the treating fluid into strata of the formation requiring treatment.

Suitably, the composition of the present invention may comprise particulate pellets of the fluid loss control agent. Where the particulate pellets are in the form of finely divided particles and are used, for example, in fracturing operation, the particles form a filter cake against the fracture face minimizing loss of the fracturing fluid to the
25 formation. After the fracturing operation is complete the particles forming the filter cake degrade and this allows the filter cake to fall away from and disperse from the fracture face resulting in an improved initial cleanup.

Particulate pellets may also be used to adjust the flow of wellbore fluid through perforations in a casing set in the wellbore. Without wishing to be bound by any theory,
30 the particulate pellets will preferentially accumulate in those perforations of the casing which communicate with formation strata having the highest permeability to the wellbore fluid thereby decreasing the flow of the wellbore fluid into the highest

permeability formation strata. Thus, the amount of pellets in the perforations communicating with the higher permeability formation strata will be greater than the amount of pellets in the perforations communicating with the least permeable formation strata.

5 It is envisaged that after completion of the well treatment, the well may be shut in for a period of time to allow the pellets to degrade before the well is put back on production. In the case of pellets comprising at least one discrete region of the first solid phase, at least one discrete region of the second solid phase and optionally at least one discrete region of a further solid phase, the rate of degradation of pellets depends, 10 amongst other things, upon the formation temperature, the size and distribution of the discrete region of the first, second and optional further solid phases in the pellets, the relative proportions of the first, second and optional further solid materials in the pellets, and the permeability of the pellets to the liquid phase of the eutectic combination. In the case of particulate pellets comprising a mixture of first pellets 15 comprising the first solid phase, second pellets comprising the second solid phase, and optionally, further pellets comprising the further solid phase, the rate of degradation of the pellets depends amongst other things on the size of the first, second and optional further pellets, the manner in which the first, second and optional further pellets pack together, for example, in a filter cake or in a perforation, and the relative proportions of 20 the first, second and optional further pellets. Depending on the size of the pellets, in most cases, it will take from about 5 hours to about 3 days for the pellets to degrade.

In a particularly preferred embodiment of the present invention there is provided a method of plugging the perforations in a casing which has been set in a wellbore which penetrates a hydrocarbon-bearing subterranean formation comprising:

25 (a) flowing down into said casing a wellbore fluid having dispersed therein particulate pellets of a fluid loss control agent, said pellets being sized to enter the perforations in the casing and being comprised of at least one discrete region of a first solid phase comprising a first solid material and at least one discrete region of a second solid phase comprising a second solid material wherein the melting points of the first and second 30 solid materials are above the temperature of the near wellbore region of the formation and the first and second solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the

temperature of the near wellbore region of the formation,

(b) continuing the flow of said wellbore fluid into the casing until at least a portion of said perforations are plugged by said pellets.

5 As discussed above the pellets may optionally comprise at least one discrete region of a further solid phase comprising a further solid material.

In yet a further particularly preferred embodiment of the present invention there is provided a method of plugging the perforations in a casing which has been set in a wellbore which penetrates a hydrocarbon-bearing subterranean formation comprising:

10 (a) flowing down into said casing a wellbore fluid having dispersed therein first and second particulate pellets of a fluid loss control agent, said first and second particulate pellets being sized to enter the perforations in the casing, said first particulate pellets comprising a first solid material and said second particulate pellets comprising a second solid material wherein the melting points of the first and second solid materials are above the temperature of the near wellbore region of the formation and the first and
15 second solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the temperature of the near wellbore region of the formation,

(b) continuing the flow of said wellbore fluid into the casing until at least a portion of said perforations are plugged by a mixture of said first and second pellets.

20 As described above, the wellbore fluid may optionally have dispersed therein further particulate pellets comprising a further solid material.

Where the wellbore fluid is a carrier fluid, step (b) of these particularly preferred embodiments of the present invention is followed by flowing a treatment fluid down the casing. This treatment fluid will be diverted into lower permeability strata of the
25 formation owing to the particulate pellets reducing the flow of the treatment fluid into the higher permeability strata.

It is also envisaged that composition of the present invention may comprise ball sealers dispersed in the wellbore fluid wherein the ball sealers comprise at least one discrete region of the first solid phase, at least one discrete region of the second solid
30 phase and optionally, at least one discrete region of the further solid phase in which case the ball sealers should be sized such that they do not enter the perforations. Instead, the flow of the wellbore fluid through the perforations carries the ball sealers to the

perforations and seats them on the perforations thereby sealing the perforations. The ball sealers are therefore held on the perforations by the pressure differential between the injected composition and the formation. The ball sealers will preferentially seal the perforations which communicate with formation strata having the highest permeability to the wellbore fluid.

As would be well known to the person skilled in the art, the composition is introduced under pressure into the casing. When the well is put back on production, it is envisaged that at least a portion of the particulate pellets or ball sealers may be removed from the perforations owing to the reversal of pressure. However, where any particulate pellets or ball sealers remain lodged in the perforations, the pellets or ball sealers will degrade over a period of time. Thus, inter-diffusion of the first, second and optional further solid materials will result in the formation of a eutectic combination comprising a liquid phase mixture of the first, second and further solid materials. This liquid phase is subsequently carried out of the wellbore with the produced fluids. Preferably, the liquid phase of the eutectic combination is dispersible or soluble in the produced fluids.

The present invention will now be illustrated by reference to the Figure.

The wellbore 1 of the Figure has a casing 2 run to the bottom of the wellbore and cemented around the outside to hold the casing 2 in place and isolate the penetrated formation. The cement layer 3 extends upward from the bottom of the wellbore at least to a point above the producing strata 5. In order for the hydrocarbon in the producing strata to be produced, it is necessary to establish fluid communication between the producing strata 5 and the interior of the casing 2 and the cement layer 3 via perforations 4.

The hydrocarbon flowing out of the producing strata 5 through the perforations 4 and into the interior of the casing 2 are transported to the surface through a production tubing 6. A production packer 7 is installed near the lower end of the production tubing 6 and above the highest perforation to achieve a pressure seal between the production tubing 6 and the casing 2. Production tubings are not always used and, in those cases, the entire interior volume of the casing is used to conduct the hydrocarbons to the surface of the earth.

When diversion is needed during a well treatment, this may be achieved by introducing the treating fluid containing the particulate pellets 8 (either pellets

comprising discrete regions of the first and second solid phases or a mixture of first and second pellets comprising the first and second solid phases respectively) dispersed therein into the casing 2 at a predetermined time during the treatment. The particulate pellets 8 can be introduced into the treating fluid either before or after the treating fluid is pumped into the upper end of the casing. Methods of accomplishing these procedures are well known in the art.

When the particulate pellets 8 are introduced into the treating fluid upstream of the perforated parts of the casing, they are carried down the production tubing 6 or casing 2 by the fluid flow. Once the fluid arrives at the perforated parts of the casing, it moves radially outward, in addition to its downward movement, toward and through the perforations 4. The flow of the treating fluid through the perforations 4 carries the particulate pellets 8 into the perforations 4. The extent to which the particulate pellets are carried into the perforations will depend upon the permeability and pressure of the producing strata 5 at each perforation. Thus, the higher the permeability or the lower the pressure of the producing strata, the higher the rate at which the treating fluid and the dispersed particulate pellets enter the perforations in communication with this strata and the greater the build up of particulate pellets in these perforations. The particulate pellets 8 are held in the perforations by the fluid pressure differential, thereby either effectively closing the perforations 4 or reducing the flow of treating fluid through the perforations until such time as the pressure differential is relieved and the pellets have either degraded or have been carried out of the perforation by the produced fluids. Ideally, the particulate pellets 8 will first enter the perforations through which the treating fluid is flowing most rapidly. This preferential closing of the perforations promotes distribution of the treatment over the entire distance of the perforations. Preferably, the well is shut in for a period of time to allow the particulate pellets to degrade before the well is put back on production. Where the particulate pellets are denser than the treatment fluid, any particulate pellets which fail to enter the perforations may fall down into the rat hole 9 where the particulate pellets will also degrade.

Claims:

1. A composition for treating a hydrocarbon-bearing subterranean formation penetrated by a wellbore which composition comprises a wellbore fluid having dispersed therein a fluid loss control agent comprising a first solid phase comprising a first solid material and a second solid phase comprising a second solid material wherein
5 the melting points of the first and the second solid materials are above the temperature of the near wellbore region of the formation and the first and second solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the temperature of the near wellbore region of the formation.
- 10 2. A composition as claimed in Claim 1 wherein the eutectic combination has a eutectic temperature at or below the temperature in the near wellbore region of the formation.
3. A composition as claimed in Claims 1 or 2 wherein the ratio of the first and second solid materials in the fluid loss control agent is at or close to the eutectic
15 composition for a mixture of the first and second solid materials.
4. A composition as claimed in any one of the preceding claims wherein the eutectic combination is capable of being formed from amongst the following combinations of first and second solid materials:
(a) the first solid material is acetaminophen and the second solid material is p-
20 aminophenol or propyphenazone;
(b) the first solid material is phenanthrene and the second solid material is benzo-(c)-cinnoline or phenanthridine;

(c) the first solid material is benzoic acid and the second solid material is selected from the group consisting of salicylic acid, acetylsalicylic acid, ethyl-p-aminobenzoate, benzamide, ethyl p-aminobenzoate and n-butyl p-hydroxybenzoate;

5 (d) the first solid material is phenacetin and the second solid material is benzamide or p-aminobenzoic acid;

(e) the first solid material is camphor and the second solid material is hydroquinone or naphthalene;

(f) the first solid material is naphthalene and the second solid material is p-dichlorobenzene or diphenylamine;

10 (g) the first solid material is poly(oxyethylene) and the second solid material is selected from the group consisting of glutaric acid, benzoic acid and 1,2-diphenylethane; and

(h) the first solid material is benzamide and the second solid material is p-chlorobenzoic acid.

5 5. A composition as claimed in Claim 4 wherein the first solid material is camphor and the second solid material is hydroquinone and the hydroquinone is present in the fluid loss control agent in an amount in the range 25 to 55 mole %, based on the total amount of camphor and hydroquinone in the fluid loss control agent.

15 6. A composition as claimed in any one of the preceding claims wherein the fluid loss control agent comprises pellets having at least one discrete region of the first solid phase and at least one discrete region of the second solid phase.

20 7. A composition as claimed in Claim 6 wherein the pellets are in the form of ball sealers having an average diameter of from 1 to 2.5 cm.

8. A composition as claimed in Claim 6 wherein the pellets are in the form of particles having an average diameter in the range 25 to 500 microns.

25 9. A composition as claimed in Claim 6 wherein the pellets are in the form of particles having a diameter of 100% less than 10 microns.

10. A composition as claimed in any one of Claims 6 to 8 wherein the pellets comprise a compressed mixture of first particles of the first solid material and second particles of the second solid material.

30 11. A composition as claimed in any one of Claims 6 to 9 wherein the pellets comprise a core of the first solid phase and a shell of the second solid phase.

12. A composition as claimed in Claim 11 wherein the shell of the second solid

phase has a thickness of from 2 to 50% of the diameter of the core of the first solid phase.

13. A composition as claimed in Claims 11 or 12 wherein the core of the first solid phase is soluble in the wellbore fluid and the shell of the second solid phase is substantially insoluble therein.

14. A composition as claimed in any one of Claims 6 to 8 wherein the fluid loss control agent comprises pellets comprising a continuous first solid phase having particles of the second solid phase dispersed therein.

15. A composition as claimed in Claim 14 wherein the particles of the second solid phase have a size of less than 150 microns, preferably less than 25 microns.

16. A composition as claimed in Claims 14 or 15 wherein the particles of the second solid phase are soluble in the wellbore fluid and the continuous first solid phase is substantially insoluble therein.

17. A composition as claimed in any one of claims 1 to 5 wherein the fluid loss control agent that is dispersed in the wellbore fluid comprises first pellets comprising the first solid phase and second pellets comprising the second solid phase.

18. A composition as claimed in Claim 17 wherein the first and second pellets are in the form of particles having a diameter of 100% less than 10 microns.

19. A composition as claimed in Claim 17 wherein the first and second pellets are in the form of particles have an average diameter in the range 25 to 500 microns.

20. A composition as claimed in any one of the preceding claims wherein the pellets are coated with a polymer which disperses in water or oil above a threshold temperature.

21. A composition as claimed in any one of Claims 1 to 5 wherein the fluid loss control agent additionally comprises at least one further solid phase comprising a further solid material wherein the first solid material, second solid material and the at least one further solid material are capable of forming a eutectic combination comprising a liquid phase mixture of the first solid material, second solid material, and the at least one further solid material at or below the temperature of the near wellbore region of the formation.

22. A method of reducing the permeability of one or more zones of a hydrocarbon-bearing subterranean formation penetrated by a wellbore which comprises introducing a

composition as claimed in any one of Claims 1 to 21 into a wellbore that penetrates said subterranean formation.

23. A method as claimed in Claim 22 wherein the wellbore fluid is a treating fluid.

24. A method as claimed in Claim 23 wherein the treating fluid is squeezed into the formation.

25. A method of plugging perforations in a casing which has been run into a wellbore which penetrates a subterranean formation comprising:

(a) flowing into said casing a wellbore fluid having dispersed therein particulate pellets of a fluid loss control agent, said pellets being sized to enter the perforations in the casing and being comprised of at least one discrete region of a first solid phase comprising a first solid material and at least one discrete region of a second solid phase comprising a second solid material wherein the melting points of the first and the second solid materials are above the temperature of the near wellbore region of the formation and the first and second solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the temperature of the near wellbore region of the formation,

(b) continuing the flow of said wellbore fluid until at least a portion of said perforations are plugged by said pellets.

26. A method as claimed in any one of Claim 25 wherein the pellets additionally comprise at least one discrete region of a further solid phase comprising a further solid material wherein the first, second and further solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first, second and further materials at or below the temperature of the near wellbore region of the formation.

27. A method of plugging the perforations in a casing which has been run into a wellbore which penetrates a subterranean formation comprising:

(a) flowing into said casing a wellbore fluid having dispersed therein first and second particulate pellets of a fluid loss control agent, said first and second particulate pellets being sized to enter the perforations in the casing, said first particulate pellets being comprised of a first solid phase comprising a first solid material and said second

particulate pellets being comprised of a second solid phase comprising a second solid material wherein the melting points of the first and the second solid materials are above the temperature of the near wellbore region of the formation and the first and second

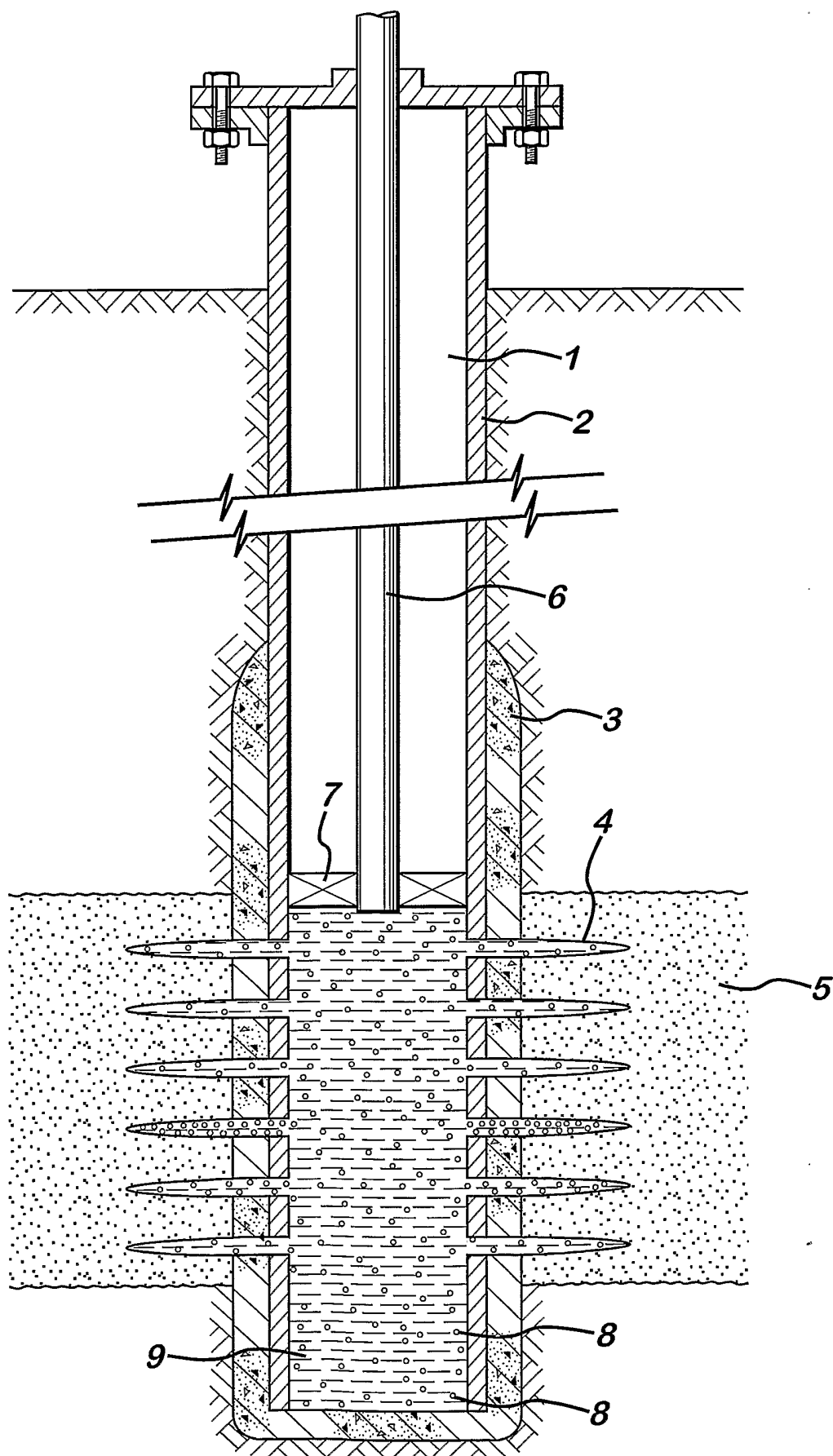
solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first and second materials at or below the temperature of the near wellbore region of the formation,

(b) continuing the flow of said wellbore fluid until at least a portion of said perforations are plugged by a mixture of said first and second pellets.

28. A method as claimed in Claim 27 wherein the fluid loss control agent additionally comprises further particulate pellets comprised of a further solid phase comprising a further solid material wherein the first, second and further solid materials are capable of forming a eutectic combination comprising a liquid phase mixture of the first, second and further materials at or below the temperature of the near wellbore region of the formation.

29. A method as claimed in any one of Claims 25 to 28 wherein the wellbore fluid is a carrier fluid and step (b) is followed by an additional step (c) of flowing a treatment fluid into the casing.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) :
IPC 7 E21B

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

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

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 797 575 A (DILL W ET AL) 19 March 1974 (1974-03-19) column 1, line 56 -column 3, line 3 claims 1-5	1-29
A	US 3 979 305 A (FISCHER PAUL W ET AL) 7 September 1976 (1976-09-07) column 1, line 55 -column 3, line 68	1-29

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- * & * document member of the same patent family

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