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(54) **Title:** FLUIDS AND METHODS

(57) **Abstract:** A method of treating a subterranean formation penetrated by a well-bore comprises the step of introducing a slurry or treatment fluid into the subterranean formation via the well-bore to plug a region of the well-bore, wherein said slurry or treatment fluid includes a diverting agent diverting agent which is suitably polylactic acid (PLA)and an additive (herein referred to as an "imbibition additive") which is suitably an acetoacetate.The diverting agent and imbibition additive interact such that the imbibition additive causes swelling of the diverting agent and/or increases the susceptibility of the diverting agent to degradation in use.

Fluids and Methods

This invention relates to fluids and methods using same. Particularly, although not exclusively, the invention relates to a method of treating a subterranean formation, a slurry and/or treatment fluid for use in the method and a method of making such a fluid. Preferred embodiments relate to use of a slurry and/or treatment fluid to facilitate fracturing of a subterranean formation.

Hydraulic fracturing is a process needed to produce oil and gas from unconventional reservoirs such as coal beds, tight sandstones and shales. In this process, a fracturing fluid is injected at rates and pressures necessary to cause formation failure by inducing fractures or cracks in the formation. These cracks originate through perforations at the well-bore and radiate out into the formation. A perforation is produced by a projectile fired from a perforating tool to create a hole through a well-bore steel casing and cement casing and into the formation, a distance 6 to 18 inches from the casing. Common practice in unconventional reservoirs is to initiate entry into the reservoir through the perforation with a small slug of acid pumped at a low rate followed by low viscosity water pumped at increasing rates until a desired high rate (typically from 50 to 100 barrels per minute) is achieved. In order to pump at these high rates, normally, small amounts of friction reducers are added to the fluid. These friction reducers are normally 120 to 1,000 ppm polyacrylamide polymers or copolymers.

Once a desired rate is achieved, a small loading of propping agent or proppant is added to the pumped fluid. Typically, most proppant comprises small-sized sand such as 0.25 pounds of 100 mesh sand per gallon of water. As a treatment proceeds, the amount of, for example, sand is systematically increased and, at some point, the size of the sand may be increased to, for example, 40/70 or 30/50 mesh. The purpose of the sand is to form a sand pack in the fracture which is orders of magnitude more permeable than the formation strata. The sand pack is then able to maintain a conductive pathway from the reservoir to the well-bore for the recovery of the reservoir fluids. Also, it is expected that the perforations in the casing are eroded. In the treatment, a perforation tunnel between the casing and the fracture is packed with proppant to produce a permeable pathway into the well-bore. Sand concentrations will normally range from 200,000 lb to 500,000 lb per fracturing stage and the water can range from 2,000 to 7,000 barrels of water.

However, the placement of transverse fractures along a horizontal lateral of a well often leaves large regions of the reservoir adjacent to the well-bore untreated, these regions being poorly fractured or poorly propped. Consequently, they contribute little or nothing to the overall oil and gas production. Such untreated regions may have initially been by-passed because of the stage intervals being excessively long or, during attempted fracturing, the treatment design may have been inadequate or relevant regions of the formation may not have taken the treating fluid.

Once a well has produced for some period of time, it may be decided to re-fracture the reservoir, particularly those regions of the formation that were poorly stimulated initially. These regions can be identified using various forms of well logging. However, re-injection of fracturing fluids, with expectations of stimulating previously untreated regions of the reservoir, is difficult without the ability to seal off those perforations that are conveying most of the production from the reservoir. To address this problem, it is desirable to introduce a temporary blocking or sealing material (a “diverting agent”) that could prevent re-injection of fracturing fluid into the most productive perforations. Once such productive perforations are sealed, treatment fluids can be injected through perforations that are less or non-productive in an effort to stimulate those regions of the reservoir. In some cases, once the most productive perforations are sealed, a new set of perforations can be formed, starting at the toe of the well and systematically working toward the heel while employing zonal isolation methods such as “plug and perf” processes.

Diverting agents may be used during a fracturing process. The first step is to stop sand or proppant addition. Once all the sand or proppant in the wellbore has cleared a perforated region of a well-bore, its injection rate may be reduced to 6 to 10 bbl/min and a diverting agent may be added in 300 to 1000 lb slugs, normally at concentrations of about 3 lb/gal of fluid. Once the diverting agent clears surface pumping equipment and enters a well head, the rate can be increased to about 20 bbl/min, but again reduced to 6 to 10 bbl/min as the diverting agent reaches the perforations. It is important the diverting agents enter the perforations at rates and pressures below fracturing pressures to seal off the perforations. The indication of a good diversion is a sudden increase in treating pressure between 200 and 1000 psi. The expectation is that diverting agents will naturally select perforations most prolific to fluid flow. Once diverting agents are set, the fracturing operations can proceed with the expectation that fluid will enter new, under-treated portions of the interval.

Although the aforementioned technique is effective, it does have certain drawbacks. For example, the addition of the 300 to 1000 lb of diverting agent (of concentration about 3lb/gal) at 6 to 10 bbl/min requires the addition to be made in 14 to 80 seconds, a feat difficult to accomplish at a well-site

In other cases, it may be desirable to inject intermittent slugs of diverting agent at lower pumping rates, while monitoring the pressure. Each time there is a pressure bump or increase after landing the diverting agent, the pumping rate on the fluid is increased to force open a new set of perforations, followed by an appropriate treating fluid volume and proppant concentration needed to fracture one or multiple zones. This is normally followed by another flush stage containing another slug of diverting agent to seal off that latest set of perforations. The fracturing stage and flush with diverting agent is repeated multiple times until the entire interval has been fractured as a means of stimulating production from previously un-fractured portions of the reservoir.

Thus, there are several requirements needed for a diverting agent. Firstly, a diverting agent should have an ability to block fluid flow at a concentration that can be operationally managed.

Secondly, a diverting agent suitably possesses some method of blocking fluid flow once a sand pack is established, such as the agent being malleable or deformable. In this mechanism, addition of pressure, sometimes influenced by temperature, will cause the product to pack and deform to block any further fluid flow, this then terminating the permeability in the flow channel.

Thirdly, another important requirement for a diverting agent is easy removal to allow continued recovery of oil and gas from previously fractured portions of the well, in addition to the newly fractured portions, to enhance ultimate recovery of oil and gas from the reservoir. This may involve self-degradation of the diverting agent. Alternatively, a mixture of diverting agent and a degrading composition may be used, with the requirement that the degrading substance becomes part of the diverting pack.

One widely used diverting agent is polylactic acid (PLA) in particulate form. The particles of PLA are expected to decompose to lactic acid oligomers within hours or days, this being relatively easily accomplished in reservoirs above 200°F. However, in cooler reservoirs, there is a problem that the rate of decomposition is too slow to be practical. It is an object of preferred embodiments of the invention to deliver PLA in a way which facilitates its decomposition, for example in relatively low temperature reservoirs.

It is an object of preferred embodiments of the present invention to address the above described problems.

According to a first aspect of the invention, there is provided a method of treating a subterranean formation penetrated by a well-bore, the method comprising the step of introducing a slurry or treatment fluid into the subterranean formation via the well-bore to plug a region of the well-bore, wherein said slurry or treatment fluid includes a diverting agent and an additive (herein referred to as an “imbibition additive”), wherein the diverting agent and imbibition additive interact such that the imbibition additive causes swelling of the diverting agent and/or increases the susceptibility of the diverting agent to degradation in use.

Said imbibition additive is preferably an organic liquid at standard temperature and pressure (STP) (i.e. at 0°C and 1 atm). Said imbibition additive may have a boiling point of greater than 120°C, for example greater than 150°C. The boiling point may be less than 300°C. Said imbibition additive may have a melting point of at least -100°C for example at least -60°C.

Said imbibition additive may have a molecular weight of at least 100 g/mol, preferably at least 120 g/mol. The molecular weight may be less than 400 g/mol, for example less than 325 g/mol or less than 250 g/mol.

Said imbibition additive may include carbon, hydrogen and oxygen atoms only.

Said imbibition additive may include an ester moiety. The ester may be an optionally-substituted alkyl (e.g. a C1-6 or C1-4 alkyl) or phenyl, ester. Said ester may be an alkyl, benzyl or phenyl ester. Whilst said ester may include more than one ester moiety (e.g two ester moieties as found in a malonate), if preferably includes a single ester moiety.

Said imbibition additive may include a ketone moiety for example an alkyl, phenyl or benzyl carbonyl moiety. It preferably includes an alkylcarbonyl moiety. A preferred alkylcarbonyl moiety may be a C1-4 alkylcarbonyl moiety, with a methylcarbonyl moiety being especially preferred. Said imbibition additive preferably includes a single ketone moiety of the type described.

In said imbibition additive, a said ketone moiety and a carbonyl group of an ester moiety are preferably separated by no more than 3 atoms and, preferably are separated by a single atom, for example a single carbon-atom.

Said imbibition additive is preferably an acetoacetate. It may be an optionally-substituted, preferably unsubstituted, benzyl, phenyl or alkyl (especially a C1-6 or C1-4 alkyl) acetoacetate. Said imbibition additive may be selected from methyl, ethyl, propyl, butyl and phenyl acetoacetate. Preferably, said imbibition additive is selected from ethyl acetoacetate and butyl acetoacetate.

The amount of imbibition additive may be selected according to the amount of diverting agent (especially PLA) in said treatment fluid. The ratio of the weight of diverting agent divided by the weight of imbibition additive may be in the range 100:1 to 5:1, preferably in the range 80:1 to 10:1, more preferably in the range 75:1 to 25:1.

The imbibition additive may be incorporated into the treatment fluid at any stage in its preparation.

Advantageously, it is found that, in use, the imbibition additive permeates particles of diverting agent (e.g. PLA) and the particles become more malleable, thereby improving their ability to pack and function as a diverting agent. Furthermore, it is found that the imbibition additive increases the rate of degradation of the diverting agent (e.g. PLA) which may be particularly relevant to formations with temperatures below 200°F. Then, the use of the imbibition additive may facilitate well clean-up particularly in relatively low temperature wells.

Thus, the method of the first aspect may comprise treating a subterranean formation wherein the temperature in a region plugged by the treatment fluid is less than 300°F, less than 250°F or less than 200°F.

The method may comprise the steps of:

(i) preparing a slurry in a process which comprises the steps of:
  (a) preparing a pre-composition which comprises an oil and one or more organic polymers suspended in the oil; and
  (b) contacting the pre-composition with water and a diverting agent; or

(ii) selecting a slurry prepared as described in step (i);

(iii) optionally contacting the slurry with an aqueous formulation thereby to prepare a treatment fluid;

(iv) including an imbibition additive in the slurry or treatment fluid at some stage during the method; and

(v) introducing the slurry or treatment fluid into the subterranean formation via the well-bore to plug a region of the formation.

Thus, for the avoidance of the doubt, the method may comprise step (i)(a), step (i)(b), step (iii), step(iv) and step(v); or may comprise step (ii), step (iii), step(iv) and step(v).

The imbibition additive may be included in step(i) or step(iii) or in a separate step.

Said oil suitably comprises a hydrophobic liquid which is suitably inert. Said hydrophobic liquid may be a hydrocarbon. It may be selected from paraffinic hydrocarbons, napthenic hydrocarbons, aromatic hydrocarbons, benzene, xylene, toluene, mineral oils, diesel oil, kerosenes, naphthas (including hydrotreated naphtha), petrolatums, branch-chain isoparaffinic solvents, branch-chain hydrocarbons, saturated, linear, and/or branched paraffin hydrocarbons and combinations thereof. Said oil may be a natural, modified or synthetic oil; or a vegetable oil such as canola oil, soy oil, coconut oil, rapeseed oil and the like.

A preferred oil may be selected from diesel, kerosene, refined mineral oils, raffinates and hydro-treated naphtha. A preferred oil is hydro-treated naphtha, preferably having a C_{11} – C_{16} carbon chain. It may have a specific gravity of 0.79 to 0.85 and a flash point exceeding 200°F.

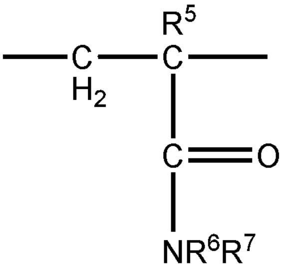
Said pre-composition may comprise 25 to 65 wt% of oil in total, for example a single type of oil which may be selected from those described. Said pre-composition preferably comprises 30 to 60 wt% of oil in total, especially 35 to 55 wt% of oil in total.

Said pre-composition may include 20 to 65 wt% of said one or more organic polymers. It preferably includes 30 to 60 wt%, more preferably 35 to 55 wt% of organic polymers.

Said one or more organic polymers in said pre-composition may include a polyacrylamide. Said pre-composition may include 10 to 40 wt%, preferably 15 to 35 wt%, more preferably 20 to 30 wt% of polyacrylamide polymers, especially a single polyacrylamide polymer.

Preferably, said polyacrylamide is an ionic polyacrylamide. Said ionic polyacrylamide may include 0.1-50mol%, preferably 5-40mol%, more preferably 10-30mol% of ionic repeat units. The balance suitably comprises non-ionic acrylamide repeat units. Whilst said polyacrylamide may be an anionic or cationic polyacrylamide, it is preferably an anionic polyacrylamide. Said polyacrylamide may be partially hydrolysed acrylamide.

Said polyacrylamide preferably includes a repeat unit which includes an optionally substituted acrylamide, for example an alkylacrylamide (e.g. methacrylamide) or N,N-dialkylacrylamide (e.g. N,N-dimethylacrylamide). Said optionally-substituted acrylamide may be of formula I



$$-CH_2-C(R^5)(C(=O)NR^6R^7)-$$

I,

wherein each R^5 independently represents a hydrogen atom or an optionally-substituted (preferably unsubstituted) C_{1-4} alkyl, preferably C_{1-2} alkyl, more preferably a methyl group and wherein R^6 and R^7 independently represent a hydrogen atom or an optionally-substituted (preferably unsubstituted) C_{1-30} alkyl, preferably C_{1-18} alkyl, preferably C_{1-12} alkyl, preferably C_{1-10} alkyl, such as a C_{1-8} alkyl, preferably C_{1-4} alkyl, preferably C_{1-2} alkyl, more preferably a methyl group.

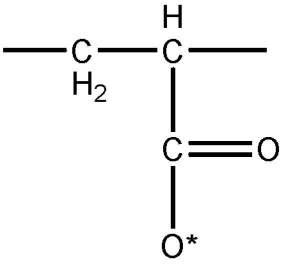
In formula I, R^5, R^6 and R^7 preferably represent hydrogen atoms.

On average, the ratio of the number of other repeat units in said polyacrylamide divided by the number of repeat units of formula I may be less than 0.6, 0.5, 0.4, 0.3 or 0.2. Said ratio may be at least 0.0025, at least 0.005, at least 0.05 or at least 0.1.

Said polyacrylamide may include (e.g. in combination with repeat unit of formula I) a repeat unit which includes an acrylate or sulfonate moiety, for example an acrylate or sulfonate salt, or a pyrrolidone moiety. Polymers which include sulfonate salts may be preferred when the formulation is used with water which includes high levels of hardness ions, for example magnesium, calcium, strontium, barium or ferrous ions.

Said polyacrylamide may include a repeat unit of formula I in combination with:

- a repeat unit comprising a moiety of formula II



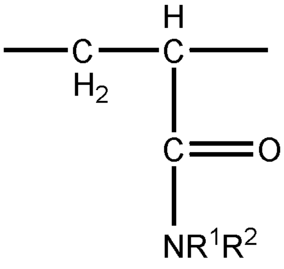
$$-CH_2-CH(C(=O)O^*)-$$

II

wherein the O* moiety is an O^- moiety or is covalently bonded to another atom or group;

- a repeat unit comprising a vinyl pyrrolidone moiety; or

- a repeat unit comprising a moiety of formula III



III

wherein R^1 and R^2 are independently selected from a hydrogen atom and an optionally-substituted alkyl group. An optionally-substituted alkyl group may define an electrically neutral hydrophobe. An optionally-substituted alkyl group may incorporate an $-SO_3R^3$ moiety wherein R^3 is selected from a hydrogen atom and a cationic moiety, for example an alkali metal cation, especially Na^+. Said optionally-substituted alkyl group may include 1 to 36, preferably 1 to 20, more preferably 1 to 10 carbon atoms. Said repeat unit may be derived from and/or based on AMPS.

Said polyacrylamide may be derived from one or more of the following monomers:

Cationic monomers - Methacryloyloxyethyltrimethylammonium chloride, Methacrylamidopropyltrimethylammonium chloride, Acryloyloxyethyltrimethylammonium chloride , Dimethyldiallylammonium chloride;

Anionic monomers - Sodium Acrylate, Sodium 2-Acrylamido-2-methylpropane sulfonate;

Non-ionic Monomers - Acrylamide, Methacrylamide, N,N Dimethylacrylamide, Vinyl pyrolidonone.

Said polyacrylamide may include monovalent (e.g. NH_4^+. Li^+, Na^+, K^+, Rb^+ or Cs^+), divalent (e.g. Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}, Cu^{2+} or Zn^{2+}) or trivalent (e.g. Fe^{3+} or Al^{3+}) cations. It preferably includes monovalent cations, with Na^+ being preferred.

Said polyacrylamide preferably includes acrylamide repeat units and acrylate, for example sodium acrylate, repeat units.

Said polyacrylamide may have a molecular weight of at least 200,000 Daltons, suitably at least 500,000 Daltons, preferably at least 1,000,000 Daltons. The molecular weight may be less than 50,000,000 Daltons or less than 30,000,000 Daltons. Molecular weight, described herein, may be measured by Measurement of Intrinsic Viscosity (see ISO 1628/1-1984-11-01); and using Intrinsic Viscosity/Molecular Weight Correlation via the Mark-Houwink Equation.

Said one or more organic polymers in said pre-composition may comprise one or more gums. Said pre-composition may include 5 to 40 wt%, preferably 15 to 30 wt% of gums in total. Said pre-composition may include one or more gums selected from a galactomannan (e.g. guar gum and locust bean gum) and xanthan gum. Said pre-composition may include 5 to 30 wt%, preferably 15 to 25 wt% of guar gum. Said pre-composition may include 1 to 10 wt% of one or more other gums. It preferably includes 2 to 7 wt%, more preferably 3 to 6 wt% of xanthan gum.

Said pre-composition may include one or more suspending agents for suspending solids in the oil. Said pre-composition may include less than 5 wt% of suspending agents in total. Said pre-composition may include 1 to 4 wt%, preferably 1.7 to 3 wt%, more preferably 2 to 3 wt% of suspending agents in total. A suspending agent (A) may be organophilic. It is preferably insoluble in said pre-composition. It is preferably a clay, for example an organophilic clay.

A said organophilic clay, which associates with oily surfaces and rejects aqueous surfaces, may be the reaction product of purified smectite clay (such as hectorite, bentonite, attapulgite, sepiolite, montmorillonate, etc.) and a quaternary ammonium salt. It includes coated clay (or lignite) such as clay coated with a fatty-acid quaternary amine. The coating imparts dispersability of the clay in the oil. Exemplary organophilic clays include those disclosed in U.S. Patent Publication No. 20070197711 and U.S. Patent Publication No. 20100305008, herein incorporated by reference. Included here are organo bentonites such as BENTONE® clays of Elementis Specialties, Inc. and Claytone SF, a product of Southern Clay Products. Further, such organophilic clays may be ion exchanged clays; see, for instance, U.S. Patent Publication No. 20010056149, herein incorporated by reference.

Said pre-composition may include at least 0.5 wt%, preferably at least 1.0 wt%, more preferably at least 1.5 wt% of organophilic clay. It may include less than 3 wt% or less than 2.5 wt% of organophilic clay.

Said pre-composition may include a suspending agent (B) which may comprise a solvent, for example a solvent arranged to activate organophilic clay. Said solvent is preferably oxygenated. It may be selected from a monohydric or polyhydric alcohol (e.g. a C_{1-6} alcohol or glycol or glycerol), a glycol ether and an organic carbonate, for example an alkylene carbonate such as propylene carbonate or glycerol carbonate.

Said pre-composition may include at least 0.1 wt% of suspending agent (B); it may include less than 5 wt% of suspending agent (B). It preferably includes 0.1 to 1.5 wt%, for example 0.2 to 1 wt% of suspending agent (B).

Said pre-composition may include a suspending agent (C) which may be a surface active agent, for example a surfactant. The pre-composition may include less than 0.5 wt%, for examples less than 0.1 wt% of suspending agent (C).

In a preferred embodiment, said pre-composition comprises:

25 to 65 wt% of oil
20 to 65 wt% of polyacrylamide polymers
5 to 40 wt% of one or more gums
0 to 5 wt% of one or more suspending agents.

Step (i)(b) may comprise contacting 1 to 10 parts by volume (pbv) of said pre-composition with 1000 parts of water. In a preferred embodiment 2 to 7 pbv, preferably 3 to 5 pbv of said pre-composition may be contacted with 1000 pbv water. Suitably, in step (i)(b), over 500 gallons or over 1000 gallons of a mixture comprising said pre-composition and water is made.

In step (i)(b), the mixture is preferably agitated to facilitate wetting and dispersion of any solids.

Said diverting agent is suitably in a particulate form, at least at the beginning of step (i)(b) of the method. Said diverting agent may be arranged to produce acid, for example after decomposition. Diverting agent may comprise, preferably consist essentially of, a polyester. Diverting agent may be selected from polyesters obtained by polymerization of hydroxycarboxylic acids, such as the aliphatic polyester of lactic acid, referred to as polylactic acid; glycolic acid, referred to as polyglycolic acid; 3-hydroxbutyric acid, referred to as polyhydroxybutyrate; 2-hydroxyvaleric acid, referred to as polyhydroxyvalerate; epsilon caprolactone, referred to as polyepsilon caprolactone or polyprolactone; the polyesters obtained by esterification of hydroxylaminoacids such as serine, threonine and tyrosine; and the copolymers obtained by mixtures of the monomers listed above. A general structure for the above-described homopolyesters is: H—{O—[C(R1,R2)]x—[C(R3,R4)]y—C=O}z—OH

where, R1, R2, R3, R4 is either H, linear alkyl, such as CH3, CH2CH3 (CH2)nCH3, branched alkyl, aryl, alkylaryl, a functional alkyl group (bearing carboxylic acid groups, amino groups, hydroxyl groups, thiol groups, or others) or a functional aryl group (bearing carboxylic acid groups, amino groups, hydroxyl groups, thiol groups, or others); x is an integer between 1 and 11; y is an integer between 0 and 10; and z is an integer between 2 and 50,000.

In the appropriate conditions (pH, temperature, water content) polyesters like those described herein can hydrolyze and degrade to yield hydroxycarboxylic acids.

Other forms of polyesters include those made by the polymerization of polycarboxylic monomers with polyhydric monomers such as oxalic acid or citric acid polymerized with ethylene glycol or glycerol, so that on hydrolysis, an acid is produced that increases the fluid acidity.

A preferred diverting agent is a polymer of lactic acid, suitably a polylactic acid (PLA), polylactate or polylactide. Lactic acid is a chiral molecule and has two optical isomers. These are D-lactic acid and L-lactic acid. The poly(L-lactic acid) and poly(D-lactic acid) forms are generally crystalline in nature. Polymerization of a mixture of the L- and D-lactic acids to poly(DL-lactic acid) results in a polymer that is more amorphous in nature. The polymers described herein are essentially linear. The degree of polymerization of the linear polylactic acid can vary from a few units (2-10 units) (oligomers) to several thousands (e.g. 2000-5000).

Said diverting agent is preferably polylactic acid (PLA).

The method may comprise contacting said diverting agent with the pre-composition after the pre-composition has been contacted with water in step (i)(b).

Said method of step (i)(b) may comprise contacting solid diverting agent with a fluid to define a slurry which includes 1 to 20 lb of diverting agent per US gallon of fluid, suitably an aqueous fluid produced by contact of said pre-composition with water. In a preferred embodiment, a slurry is defined which includes 3 to 10 lb, more preferably 5 to 9 lb, especially 6.5 to 8.5 lb, of diverting agent per US gallon of fluid, as described.

Presented another way, said method of step (i)(b) may comprise contacting solid diverting agent with fluid to define a slurry which includes 0.12 to 2.38 kg (preferably 0.36 to 1.19 kg, more preferably 0.59 to 1.07 kg, especially 0.77 to 1.01 kg) of diverting agent per litre of fluid as described.

The method may comprise preparing a treatment fluid which includes 0.003 to 0.066 kg (preferably 0.005 to 0.033 kg, especially 0.008 to 0.0290 kg) of imbibition additive per litre of fluid as described.

Said slurry may include a cross-linker for cross-linking polymer(s) included the slurry.

Said slurry may include a viscosifying agent (which may be defined at least in part by said organic polymers) which is suitably arranged to suspend particulates in the slurry. The viscosifying agent may comprise any crosslinked polymer. The viscosifying agent may be a metal-crosslinked polymer. Suitable polymers for making a metal-crosslinked polymer viscosifier include, for example, polysaccharides such as substituted galactomannans, such as guar gums, high-molecular weight polysaccharides composed of mannose and galactose sugars, or guar derivatives such as hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG) and carboxymethyl guar (CMG), hydrophobically modified guars, guar-containing compounds, and synthetic polymers. Crosslinking agents based on boron, titanium, zirconium or aluminum complexes are typically used to increase the effective molecular weight of the polymer and make the viscosifying agent better suited for use in high-temperature wells, for example for carrying solids (e.g. proppant or other diverting agents) in the treatment of subterranean formations.

Other suitable classes of polymers effective as viscosifying agents include polyvinyl polymers, polymethacrylamides, cellulose ethers, lignosulfonates, and ammonium, alkali metal, and alkaline earth salts thereof. More specific examples of other typical water soluble polymers are acrylic acid-acrylamide copolymers, acrylic acid-methacrylamide copolymers, polyacrylamides, partially hydrolyzed polyacrylamides, partially hydrolyzed polymethacrylamides, polyvinyl alcohol, polyalkyleneoxides, other galactomannans, heteropolysaccharides obtained by the fermentation of starch-derived sugar and ammonium and alkali metal salts thereof. Cellulose derivatives, such as hydroxyethylcellulose (HEC) or hydroxypropylcellulose (HPC), carboxymethylhydroxyethylcellulose (CMHEC) and carboxymethycellulose (CMC), may be used, with or without crosslinkers, as may xanthan, diutan, and scleroglucan.

Said slurry and/or treatment fluid may be arranged to define a sealing composition which is introduced into the subterranean formation in step (iv) of the method. The method preferably comprises allowing the slurry and/or treatment fluid to form a degradable seal in the subterranean formation. Preferably, the slurry and/or treatment fluid is arranged to degrade over time.

Whilst in some embodiments, said slurry could be introduced into the formation without dilution, it is preferred that the slurry is contacted with an aqueous formulation, thereby to prepare a said treatment fluid which is suitably introduced into the formation. The aqueous formulation with which the slurry is contacted may be an injection fluid or may be another source of water which may be fresh water or produced water.

Said treatment fluid introduced into the subterranean formation in step (iii) may include:

- 10 to 69.99 wt% diverting agent, especially PLA;
- 0.10 to 2.0 wt% of imbibition additive, especially an acetoacetate;
- 30 to 89.99% of water; and
- 0 to 5 wt% of other components, for example ingredients of the pre-composition described herein.

Said treatment fluid may include:

- 20 to 59.99 wt%, preferably 30 to 39.99 wt%, of diverting agent, especially PLA;
- 40 to 79.99 wt%, preferably 60-69.99 wt, of water
- 0.57 to 1.71 wt% preferably 0.86 to 1.14% of imbibition additive, especially selected from methyl, ethyl, propyl, butyl and phenyl acetoacetate.

Said treatment fluid may include less than 2 wt% or less than 1 wt% of other ingredients.

Preferably, in said treatment fluid, the sum of the wt% of diverting agent, especially PLA, imbibition additive and water is at least 97 wt%, at least 98 wt% or at least 99 wt%.

Preferably, in said treatment fluid, the sum of the wt% of ingredients described herein as being in said pre-composition is less than 1 wt%, preferably less than 0.1 wt%.

Preferably, in said treatment fluid, the wt% of polyacrylamide(s) (e.g. as described) is less than 1 wt%, more preferably, less than 0.5 wt %, especially less than 0.1 wt%.

Preferably, in said treatment fluid, the wt% of guar is less than 1 wt%, more preferably less than 0.5 wt%, especially less than 0.1 wt%.

The method of the first aspect suitably comprises a method of hydraulic stimulation of the subterranean formation. The method may comprise introducing fluid, for example said treatment fluid into a first fracture in the formation, suitably so the fluid, for example said treatment fluid containing diverting agent at least partially hydraulically isolates the first fracture. Subsequently, the subterranean formation may be stimulated with a stimulation fluid (e.g. a fracturing fluid) sufficient to create and/or extend a second fracture within the formation. The resulting diverting agent seal (produced by fluid introduced into the first fracture) may then degrade. As a result, at least some of the fluid introduced flows from the first fracture into the wellbore.

The method may comprise introducing fluid, for example treatment fluid into at least 2, preferably at least 3 or at least 4 fractures. After said introduction, at least 2 or at least 3 other fractures may be created and/or expanded.

At some stage in the method, fluid, for example treatment fluid, introduced into the formation, may include one or a plurality of proppants. The proppant may have a size of at least 140 US mesh; it may have a size of less than 5 US mesh. The proppant may be selected from sand, bauxite, and man-made intermediate or high strength materials.

At some stage in the method, a said treatment fluid introduced into the formation includes at least 2.9wt%, for example at least 5wt%, of proppants. Higher percentages of proppants may be used as a treatment progresses.

The fluid, for example treatment fluid introduced in step (iv) is preferably pumped to re-fracture producing wells, but can be part of an initial fracturing treatment before a well is placed into production to get better distribution of proppant along the entire interval.

In either case, in step (iv), the injection rate of fluid into the formations is preferably in the range to 6 to 10 bbl/min. In most cases, the number of open perforations is determined from the injection pressure. Once the number of perforations is determined, a portion of the open perforations will be taking a majority of the fracturing fluid. This can be 5 to 50% of the perforation, but more often is 10 to 60% and most often is 20 to 30%.

The imbibition additive is suitably a solvent as described herein.

The use of the imbibition additive (e.g. solvent) may be particularly beneficial when the formation temperature is less than 200°F (93°C). The imbibition additive (e.g. solvent) makes the diverting agent more malleable and/or more susceptible to degradation. In addition, post treatment of the diverter pack in the well-bore with an oxidizing agents like sodium or ammonium persulfate at concentrations ranging from 2.0 to 20 lb per 1000 gallons (ppt) oxidizer can easily degrade the outer skin of the diverting agent. This removes the more malleable portions of the particles, so the particles in the pack can be released from the pack by fluid flow from the fracture flow and eventually recovered on the surface.

The invention extends to a method of fracturing a subterranean formation, the method comprising:

- introducing said slurry or treatment fluid into the subterranean formation via the well-bore to plug a region of the formation;

- fracturing said formation to produce a fracture in a region of said formation different to said region which is plugged by said slurry or treatment fluid;

- wherein after said fracturing at least part of said slurry or said treatment fluid which plugs the region is at least partially removed.

According to a second aspect of the invention, there is provided a slurry or treatment fluid as described in the first aspect. The slurry may be as described in step (i) and/or is a treatment fluid which is introduced in step (iv) of the first aspect.

The slurry and/or treatment fluid may include any feature of the slurry and/or treatment fluid of the first aspect.

Said slurry and/or treatment fluid may be a combination of the pre-composition, water, diverting agent and imbibition additive as described in the first aspect.

According to a third aspect of the invention, there is provided a process for preparing a slurry or treatment fluid for treating a subterranean formation, the process comprising the steps of:

(a) preparing a pre-composition which comprises an oil and one or more organic polymers suspended in the oil;

(b) contacting the pre-composition with water and a diverting agent; and

including in the slurry or treatment fluid an imbibition additive as described.

Said imbibition additive may be added in step(a), step(b) or in a separate step.

The process of the third aspect may include any feature of the method described in the first aspect.

Any feature of any aspect of any invention described herein may be combined with any feature of any other aspect of any invention described herein mutatis mutandis.

Specific embodiments of the invention will now be described, by way of example.

The following materials are referred to hereinafter.

MaxPure™ PD210 – a petroleum hydro-treated middle distillate with CAS number being 64742-46-7.

Claytone™ SF – an organophilic clay used as the oil-carrier suspending agent.

Lutensol™ TDA9 – a surfactant to assist polymer hydration once the slurry is added to water.

Guar 40-45 – a guar gum grade that will provide a Fann 35 viscosity of 40 cP at 511 sec^{-1} in 3 minutes after mixing a 0.48 wt% concentration in water in a Waring blender shearing at 2000 rpm for 2 minutes. The grade also provides 45 cP at the same shear rate after 60 minutes.

Flojet™DRP 3015 - an ultra-fine grind high molecular weight 30% anionic polyacrylamide.

VisLink200™- a borate based cross-linker from Innospec Oilfield Services™.

Any reference to non-SI units herein such as gallons, refer to units used in the United States.

In general terms, preferred embodiments relate to aqueous, high density slurry formulations comprising a high concentration of diverting agent particulate, for example multi-sized polylactic acid (PLA). In preparation of the aqueous slurry formulation, a pre-composition is prepared. This may comprise an oil-based slurry comprising suspending polymers and suspending agents. For example, the oil-based slurry may comprise polyacrylamide, guar gum and xanthan gum, as suspending polymers together with suspending agents. This may be relatively easily metered and mixed into water to produce an aqueous formulation into which the diverting agent particulate may be introduced. The slurry also includes a solvent (e.g. an ester of acetoacetate) which the PLA particles imbibe. The slurry may optionally be diluted with water. Thereafter, the fluid may be introduced into a subterranean formation so as to block perforations in the formation and allow other parts of the formation to be fractured.

The invention is described in more detail below.

The pre-composition in the form of an oil-based slurry may include any oil commonly used to create oilfield oil-based slurries. It may include diesel, kerosene, refined mineral oils, raffinates and hydro-treated naphtha. A preferred oil is hydro-treated naphtha having a C_{11} – C_{16} carbon chain and a specific gravity of 0.79 to 0.85 and a flash point exceeding 200°F.

The pre-composition may include 35 to 65 wt% of oil in total. It preferably includes 40 to 60 wt% or, more preferably, 45 to 55 wt% of oil in total, wherein the oil(s) may be selected from those stated.

The pre-composition may include one or more suspending agents which are suitably arranged to facilitate suspension of diverting agent particulates (e.g. PLA) when provided in the aqueous formulation.

In a preferred embodiment, the pre-composition comprises three suspending agents - an organophilic clay, an activating solvent and a surfactant. The organophilic clay can be any organophilic clay that provides suspension to the particulates in the aqueous slurry formulation. Suitable clays include Bentone™ 150 and Bentone™ 155 from Elementis™ or Claytone™ EM, Claytone™ AF and Claytone™ SF™.

The activating solvent can be any oxygenated solvent that can activate the organophilic clays and may include C1 to C6 alcohols, glycol ethers and organic carbonates.

The surfactant can be any non-ionic surfactant having a hydrophobic group with 6 to 24, for example 9 to 16 carbon atoms, and a degree of ethoxylation ranging from 6 to 18, for example 6 to 12.The HLB of the surfactant may range from 11 to 15.

The concentration of the organophilic clay in the pre-composition may be in the range from 1 wt% to 3wt%, preferably 1.25 wt% to 2.75 wt% and, especially, 1.50 wt% to 2.00 wt%.

The total amount of activating solvent in the pre-composition may be in the range 0.0 wt% to 1.0 wt%, preferably in the range 0.25 wt% to 0.75 wt% and, especially in the range 0.3 wt% to 0.5 wt%.

The total amount of surfactant in the pre-composition may be in the range 0 wt% to 1 wt%, preferably in the range 0 wt% to 0.5 wt% and, especially, in the range 0 wt% to 0.2 wt%.

The suspending polymers in the pre-composition may comprise a mixture which comprises one or more of a galactomannan (e.g guar gum), xanthan gum and polyacrylamide.

The polyacrylamide is high molecular weight exceeding 10 MM g/mole in number average molecular weight, preferably 12 MM g/mole and most preferred exceeding 15 MM g/mole molecular weight. A preferred polymer is also useful as a hydraulic fracturing friction reducer and may be composed of 10% to 40% (mole percent) of anionic acrylate to enhance polymer expansion and viscosity in water. The size distribution may be small with a mean size of 150 µm. The concentration in the slurry can range from 10wt% to 40wt% and more preferred from 15wt% to 35wt% and most preferred from 20wt% to 30wt%.

The xanthan gum may be any type useful as a rheology modifier and exhibiting high yield stresses. The gum can be acylated or non-acylated. The concentration can range from 0wt% to 10wt% and more preferred from 2wt% to 8wt% and most preferred from 4wt% to 6wt%.

The galactomannan may be selected from guar gum and locust bean gum. The guar gum can be any fracturing grade guar gum. Guar gum is normally graded by its 3 minute and 60 minute hydration viscosity using 0.48wt% polymer in 500 ml of 2wt% KCl water sheared at 2,000 rpm for 2 minutes in a Waring™ blender and poured into a Fann™ 35 viscometer cup with an R1B1 rotor/bob assembly to be sheared at 511 sec^{-1}. A guar gum having a viscosity of 36 cP in 3 minutes and 42 cP in 60 minutes is graded as a 3642 grade guar. In preferred embodiments, the higher the grade the better the suspension so that Grade 3642 works well, but Grade 4045 works better and 4552 works best as a suspending polymer.

A specific example of a pre-composition which may be used in preparing the slurry formulation is as follows. Note that the order of materials presented in the table represents the order of addition used in preparing the pre-composition, but the guar gum, xanthan gum and polyacrylamide polymers can be added in any order.

Material	Wt%	grams
MaxPure PD210	48.96	48.960
Claytone SF	2.09	2.090
Propylene carbonate	0.46	0.460
Lutensol TDA 9	0.01	0.010
Guar 40-45	19.46	19.460
Xanthan	4.40	4.400
FLOJET DRP 3015	24.62	24.620

An aqueous, high-density slurry formulation can be made using the pre-composition either in a manufacturing plant, at a well-site or at any place conducive to mixing large volumes of aqueous slurries, whichever is convenient based on slurry volumes or well-site operational logistics.

The pre-composition is added to any fresh water having a Total Dissolved Solids (TDS) of under 4,000 ppm and hardness under 1000 ppm. The amount of water is selected to deliver a desired amount of diverting agent to perforations in a subterranean formation.

The pre-composition can be added to the water in either a continuous manner to a flowing stream of water or in a batch-wise manner with good agitation to assist hydration of polymers in the pre-composition. An advantage of the pre-composition is its ability to disperse in the water prior to hydration to prevent lumping or “fish-eyes”. Typical loadings can range from 1 to 6 gallons pre-composition per 1000 gallon of water (i.e. gallons per thousand or gpt). More preferred is 1.5 to 5.0 gpt and most preferred is 2.0 to 4.0 gpt.

Once the polymers in the pre-composition are hydrated, the diverting agent can be added to the polymer solution. It is preferred to keep the minimum concentration of diverting agent greater than or equal to 3 lb/gal. In this case, for 1000 gal of polymer solution, at least 4,200 lb of diverter is necessary.

Any diverting agent can be used that is immiscible with water and will either slowly degrade or can be removed later with a degrading fluid. Later removal may involve the addition of a strongly oxidizing agent to flush the well-bore after a fracturing treatment such as after the plug drill out process if a “plug and perf” process was used for zonal isolation but before well-cleanup. In addition, it is preferred for the diverting agent to be slightly malleable to seal off fluid flow through the perforation. A preferred chemical diverting agent is sized polylactic acid. A typical size distribution of a preferred PLA is shown in the Table 1.

Table 1

Polylactic Acid Particle Size Analysis	
Mesh Size	**% Retained (by wt)**
20	0.0
30	9.3
35	18.3
40	16.1
45	13.4
50	10.5
60	8.5
70	4.3
80	4.5
100	4.5
Pan	10.6
Mean Particle Diameter (mm)	0.387
Median Particle Diameter (mm)	0.319

An additional solvent is included in the aqueous slurry formulation and arranged to permeate the PLA particles. The additional solvent may be an ester of acetoacetate, such as methyl, ethyl, propyl, butyl and phenyl acetoacetate. The most preferred are ethyl and butyl acetoacetate.

The ester of acetoacetate may be added to the slurry formulation (or a precursors) before, during or after addition of the PLA. Typically, when for example butyl acetoacetate is added 1 part being weight of the acetate may be added per part by weight of the PLA.

The aqueous slurry formulation can also include one or more biocides to extend its life. Biocide may be added at any time during slurry preparation. For example, biocide may be added to water added to the pre-composition; to the mixture prepared just before addition of the diverting agent; or it may be added after addition of the diverting agent.

Typical biocides include tetrakis (hydroxymethyl) phosphonium sulfate, methyl or chloro isothiazolone, glutaraldehyde, quaternary ammonium-based surfactants such as didecyldimethyl ammonium chloride and mixtures of glutaraldehyde and didecyldimethylammonium chloride. Common mixtures can be 12wt% glutaraldehyde 3wt% didecyldimethylammonium chloride.

The slurry formulation can be pumped alone as a treating fluid itself or diluted with injection (or other aqueous) fluid, with the proviso that the diverting agent concentration preferably remains greater than or equal to 3.0 lbs of diverter per gallon of fluid. If diluted, this water can be fresh water, flow-back water from other previously fractured wells or produced water with the water quality, expressed as ppm of Total Dissolved Solids (TDS), to not exceed 100,000 ppm.

The amount of slurry formulation required depends on the expected number of perforations taking fluid. In general 3 to 5 lbs diverting again may be used per perforation.

Treating fluid including the slurry formulation is suitably injected at a pump rate between 6 and 10 bbl/min until the slurry slug clears the well head. The rate can then increase to 20 bbl/min until the slug reaches the perforation. The slurry rate is then dropped to less than 10 bbl/min with a pressure of placement below that needed to fracture the well.

In a specific embodiment, 7.5 lb of PLA is added to 1.0 gallons of the pre-composition and additional water added to form an aqueous based diverter slurry (ABDS). It has been found, in preferred embodiments, that the maximum amount of PLA should be no greater than 7.5 lb PLA per gallon of pre-composition

Based on the aforesaid, the table below shows, for a range of pump rates, the volume of ABDS and additional water needed to make a fluid which is injected into a well.

Assuming 7.5 ppga of diverting agent in ABDS to maintain 3 ppg PLA in treating fluid			Component wt% in the treating fluid					
Rate (BPM)	ABDS (BPM)	Water (BPM)	% PAm	% Guar	% Xanthan	% PLA	% Oil	% t-BAA
6.0	4.1	1.9	0.068%	0.054%	0.012%	35.1%	0.136%	0.69%
6.5	4.4	2.1	0.068%	0.054%	0.012%	34.8%	0.135%	0.69%
7.0	4.8	2.2	0.069%	0.054%	0.012%	35.2%	0.136%	0.70%
7.5	5.1	2.4	0.068%	0.054%	0.012%	34.9%	0.135%	0.69%
8.0	5.5	2.5	0.069%	0.054%	0.012%	35.3%	0.137%	0.70%
8.5	5.8	2.7	0.068%	0.054%	0.012%	35.0%	0.136%	0.69%
9.0	6.2	2.8	0.069%	0.054%	0.012%	35.4%	0.137%	0.70%
9.5	6.5	3.0	0.068%	0.054%	0.012%	35.1%	0.136%	0.69%
10.0	6.8	3.2	0.068%	0.054%	0.012%	34.9%	0.135%	0.69%

The slurry formulation may include about 0.7wt% of butyl acetoacetate.

Note, in the slurry formulation, the balance of wt% is mostly water.

It may be possible to reduce the amount of PLA in the ABDS to be equivalent to 3 lb PLA per gallon of ABDS. In this case, the PLA concentration would be 4.2 lb PLA to 7 a gallon of the pre-composition used to make the ABDS. In this case, for each pump rate, the ABDS could be used as the treating fluid without the need for additional water.

The slurry formulation described, including the acetoacetate, may be particularly useful for treating reservoirs with temperatures below 200°F. In such reservoirs, without the acetoacetate, the polylactic acid particulates degrade too slowly and the temperature is too low to induce the needed malleability to seal the perforations. However, the acetoacetate will permeate the particles to make them more malleable, and, furthermore, assists in the particle degradation to allow improved well clean-up.

The efficiency of imbibition of the acetoacetate can be improved by increasing the salinity of the water used in the slurry formulation. Salinity can be increased by the addition of sodium chloride. .

The slurry formulation can readily be prepared and used at suitable concentrations. It is found to provide an improved seal and be more easily cleaned up compared to an equivalent slurry formulation to that described (except that it does not include an ester of acetoacetate such as t-butyl acetoacetate.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed. .

CLAIMS

1 A method of treating a subterranean formation penetrated by a well-bore, the method comprising the step of introducing a slurry or treatment fluid into the subterranean formation via the well-bore to plug a region of the well-bore, wherein said slurry or treatment fluid includes a diverting agent and an additive (herein referred to as an “imbibition additive”), wherein the diverting agent and imbibition additive interact such that the imbibition additive causes swelling of the diverting agent and/or increases the susceptibility of the diverting agent to degradation in use.

2 A method according to claim 1, wherein said imbibition additive is an organic liquid which has a boiling point of greater than 120°C and less than 300°C; and a melting point of at least -100°C.

3 A method according to claim 1 or claim 2, wherein said imbibition additive includes carbon, hydrogen and oxygen atoms only.

4 A method according to any preceding claim, wherein said imbibition additive includes an ester moiety, for example an optionally-substituted alkyl (e.g. a C1-6 or C1-4 alkyl) or phenyl, ester.

5 A method according to any preceding claim, wherein said imbibition additive includes a ketone moiety.

6 A method according to any preceding claim, wherein in said imbibition additive, a said ketone moiety and a carbonyl group of an ester moiety are separated by a single carbon-atom.

7 A method according to any preceding claim, wherein said imbibition additive is an acetoacetate.

8 A method according to any preceding claim, wherein said imbibition additive is selected from methyl, ethyl, propyl, butyl and phenyl acetoacetate.

9 A method according to any preceding claim, wherein the ratio of the weight of diverting agent divided by the weight of imbibition additive is in the range 100:1 to 5:1, preferably in the range 75:1 to 25:1.

10 A method according to any preceding claim, wherein the method comprises treating a subterranean formation wherein the temperature in a region plugged by the treatment fluid is less than 300°F, less than 250°F or less than 200°F.

11 The method may comprise the steps of:

(i) preparing a slurry in a process which comprises the steps of:
(a) preparing a pre-composition which comprises an oil and one or more organic polymers suspended in the oil; and
(b) contacting the pre-composition with water and a diverting agent; or

(ii) selecting a slurry prepared as described in step (i);

(iii) optionally contacting the slurry with an aqueous formulation thereby to prepare a treatment fluid;

(iv) including an imbibition additive in the slurry or treatment fluid at some stage during the method; and

(v) introducing the slurry or treatment fluid into the subterranean formation via the well-bore to plug a region of the formation.

12 A method according to claim 11, wherein said oil is selected from a hydrocarbon or a vegetable oil; and is preferably selected from diesel, kerosene, refined mineral oils, raffinates and hydro-treated naphtha.

13 A method according to claim 11 or claim 12, wherein said pre-composition comprises 25 to 65 wt% of oil in total, for example 35 to 55 wt% of oil in total.

14 A method according to any of claims 11 to 13, wherein said pre-composition includes 20 to 65 wt% of said one or more organic polymers, preferably 35 to 55 wt% of said organic polymers.

15 A method according to any of claims 11 to 14, wherein said one or more organic polymers in said pre-composition include a polyacrylamide; and said pre-composition includes 10 to 40 wt% of polyacrylamide polymers.

16 A method according to any of claims 11 to 15, wherein said one or more organic polymers in said pre-composition comprises one or more gums; wherein said pre-composition includes 5 to 40 wt% of gums in total.

17 A method according to any of claims 11 to 16, wherein said pre-composition includes 5 to 30 wt%, preferably 15 to 25 wt%, of guar gum and, optionally, 1 to 10 wt% of one or more other gums, for example xanthan gum.

18 A method according to any of claims 11 to 17, wherein said pre-composition includes a suspending agent (A) which is an organophilic clay, wherein said pre-composition includes at least 0.5 wt% and 3 wt% or less of organophilic clay.

19 A method according to any of claims 11 to 18, wherein said pre-composition comprises:

25 to 65 wt% of oil;
20 to 65 wt% of polyacrylamide polymer(s);
5 to 40 wt% of one or more gums; and
0 to 5 wt% of one or more suspending agents.

20 A method according to any of claims 11 to 19, wherein step (i)(b) comprises contacting 1 to 10 parts by volume (pbv) of said pre-composition with 1000 parts of water.

21 A method according to any of claims 11 to 20, wherein said method of step (i)(b) comprises contacting solid diverting agent with fluid to define a slurry which includes 0.12 to 2.38 kg (preferably 0.36 to 1.19 kg, more preferably 0.59 to 1.07 kg, especially 0.77 to 1.01 kg) of diverting agent per litre of pre-composition.

22 A method according to any preceding claim, wherein said diverting agent is arranged to produce acid.

23 A method according to any preceding claim, wherein said diverting agent comprises a polyester.

24 A method according to any preceding claim, wherein said diverting agent is polylactic acid (PLA).

25 A method according to any preceding claim, which comprises preparing a treatment fluid which includes 0.003 to 0.066 kg (preferably 0.005 to 0.033 kg, especially 0.008 to 0.0290 kg) of imbibition additive per litre of fluid, for example slurry and/or treatment fluid.

26 A method according to any preceding claim, wherein said method comprises a method of hydraulic stimulation of the subterranean formation and comprises introducing treatment fluid into a first fracture in the formation, so the treatment fluid containing diverting agent at

least partially hydraulically isolates the first fracture; and, subsequently, the subterranean formation is stimulated with a stimulation fluid to create and/or extend a second fracture within the formation.

27 A slurry or treatment fluid as described in any preceding claim per se.

28 A process for preparing a slurry or treatment fluid for treating a subterranean formation, the process comprising the steps of:

(a) preparing a pre-composition which comprises an oil and one or more organic polymers suspended in the oil; and

(b) contacting the pre-composition with water and a diverting agent; and

including in the slurry or treatment fluid an imbibition additive.

29 A process according to claim 28 which includes any feature of the method described in step (i) in any of claims 1 to 26.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/050203

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/68 C09K8/88 C09K8/90
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/065975 A1 (HALLIBURTON ENERGY SERV INC [US]) 1 May 2014 (2014-05-01)	1-6,9, 10,22-27
Y	claims paragraph [0046] paragraph [0076] -----	11-21, 28,29
Y	WO 2016/201445 A1 (UNIVAR USA INC [US]) 15 December 2016 (2016-12-15) claims -----	11-21, 28,29
Y	US 5 067 566 A (DAWSON JEFFREY C [US]) 26 November 1991 (1991-11-26) claims 1,6 -----	7,8
Y	US 2005/037928 A1 (QU QI [US] ET AL) 17 February 2005 (2005-02-17) claims 1, 16, 17 -----	7,8

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 20 March 2019	Date of mailing of the international search report 29/03/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Zimpfer, Emmanuel

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2019/050203

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