Title: HYDRATEABLE POLYMER SLURRY AND METHODS FOR MAKING AND USING SAME

Abstract: A water-free slurry may include a non-aqueous carrier fluid; a suspension agent including a mineral clay mixture; and hydratable polymer microbeads. A method of treating a subterranean formation may include mixing an aqueous fluid with a water-free slurry to create a mixed fluid; the water-free slurry including a non-aqueous carrier fluid; a suspension agent including a mineral clay mixture; and hydratable polymer microbeads; and circulating the mixed fluid through a wellbore penetrating the subterranean formation.

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HYDRATABLE POLYMER SLURRY AND METHODS FOR MAKING
AND USING SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present document is based on and claims priority to U.S. Provisional Application Serial No.: 62/182,898, filed June 22, 2015, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] In subterranean water shut-off treatment operations, high viscosity fluids are formulated using dry synthetic polymers which are mixed with water or other aqueous fluids at the job site. Such commercial mixing procedures are known to involve inherent problems, particularly on remote sites or when large treatment volumes are required. For example, special equipment for mixing the dry additives with water may be required and problems such as chemical dusting, uneven mixing, lumping of the gels while mixing and extended preparation and mixing times may be observed. Further, the mixing and physical handling of large quantities of dry chemicals require a great deal of manpower, and when continuous mixing is required, the accurate and efficient handling of dry chemicals is extremely difficult. Also, with respect to batch mix applications, the occurrence of job delays can result in the deterioration of premixed gels and potential loss thereof as well as chemical losses due to tank bottoms and problems associated with the cost of pretreatment tank clean ups.

[0003] To overcome some of these issues, hydratable synthetic polymers have been supplied in a non-aqueous slurry concentrate which is useful in continuous processes supplying a viscous, gelled aqueous fluid for subterranean water-shut-off treatment. Such a slurry concentrate typically involves a synthetic polymer slurry wherein a hydratable polymer is dispersed in a hydrophobic solvent (e.g. an oil-based fluid) in combination with a suspension agent and an activator. The hydratable polymer may disperse evenly when added to the hydrophobic oil-based solvents. The even dispersion
tends to eliminate lumping and premature gelation problems and tend to optimize the initial dispersion of the hydratable polymer when added to water.

[0004] Once the polymer is dispersed, its ability to absorb water will dictate its hydration time and hydration rate. The hydration of the polymer is still an important factor particularly in continuous mix applications wherein the hydration and associated viscosity rise should take place over a relatively short time span corresponding to the residence time of the fluids during the continuous mix procedure. A variety of techniques exist for controlling the hydration of the hydratable polymer. For example, hydration rate can be controlled by the level of applied shear, with the hydration, and correspondingly the solution viscosity, increasing faster when subjected to high shear. Additionally, the use of finely divided polymer particles, such as those capable of passing through a 200-mesh Tyler screen (or finer), has been used to improve hydration rate and also in order to form a stable suspension of the hydratable polymer in the hydrophobic oil-based solvent.

SUMMARY

[0005] In one aspect, embodiments disclosed herein relate to a water-free slurry that includes a non-aqueous carrier fluid; a suspension agent including a mineral clay mixture; and hydratable polymer microbeads.

[0006] In another aspect, embodiments disclosed herein relate to a method of treating a subterranean formation that includes mixing an aqueous fluid with a water-free slurry to create a mixed fluid, the water-free slurry including a non-aqueous carrier fluid; a suspension agent including a mineral clay mixture; and hydratable polymer microbeads; and circulating the mixed fluid through a wellbore penetrating the subterranean formation.

[0007] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS
FIG. 1 shows a plot of rheology over time for samples tested in Example 5.

FIG. 2 shows a plot of rheology over time for samples tested in Example 5.

DETAILED DESCRIPTION

Embodiments disclosed herein generally relates to water-free oil or solvent-based suspensions/slurries of hydratable polymer for water or gas conformance control. More specifically, the water-free suspension/slurry may include hydratable polymer, a suspending agent, a polymeric suspension stabilizer, and a carrier fluid.

In one or more embodiments, the hydratable polymer may be any watersoluble, viscosity-enhancing polymer or mixture of polymers generally known in the art to yield an increase in viscosity upon hydration. Thus, hydratable polymers may include polyacrylamide and acrylamide copolymers thereof including acrylamide sodium acrylate copolymer, any natural or modified natural polymers including polysaccharides and modified polysaccharides and related polymeric materials such as guar, hydroxypropyl guar (HPG), hydrophobically modified hydroxypropyl guar (HMHPG), carboxymethyl guar (CMG), carboxymethyl hydroxypropyl guar (CMHPG), carboxymethyl hydroxyethyl cellulose (CMHEC), carboxymethylcellulose, other cellulosics and cellulolic derivatives such as hydroxyethylcellulose and hydroxypropylcellulose; xanthan gum, modified starches, glucomannan gums, succinoglycan, scleroglucan, o-carboxychitosans, polyvinylsaccharides, heteropolysaccharides (such as diutan by nonlimiting example, and similar biopolymers and mixtures thereof.

In one or more embodiments, the hydratable polymer may be in the form of microbeads. More specifically, in one or more embodiments, a majority of the hydratable polymer microbeads may have diameters greater than about 100 microns, or greater than about 200 microns, or greater than about 300 microns. In one or more embodiments, the hydratable polymer microbeads may have a $d_{10}$ of at least 150 microns. In one or more embodiments, the hydratable polymer may have a $d_{50}$ of at least about 300 microns and up to about 425 microns. In one or more embodiments, the hydratable polymer may have a $d_{90}$ of at least about 425 microns and up to 1000 microns, or up to 600 microns.
Traditionally, and even though they may have a more flowable morphology and avoid
dusting problems during their slurrification, hydratable polymers in the form of
microbeads have not found use in water-free oil or solvent-based suspensions because of
issues with suitably suspending the hydratable polymer and also ensuring its rapid
hydration upon mixing with water-based fluids.

[0013] In one or more embodiments, the hydratable polymer may be included in the
water-free slurry in an amount ranging from about 5% to 70% by weight of the water-free
slurry, or from about 10% to 65% by weight of the water-free slurry, or from about 15% to
60% by weight of the water free slurry, or from about 20% to 55% by weight of the
water free slurry.

[0014] In the present disclosure, a suspending agent may be used to provide viscosity
and thixotropic properties to the suspension so that the suspended hydratable polymer
particles are prevented from settling. In one or more embodiments, the suspending agent
may be a mineral clay mixture and more particularly an organophilic mineral clay
mixture. In one or more embodiments, the mineral clay mixture may be treated with
alkyl quaternary ammonium compounds in order to render the mineral clay mixture
hydrophobic; such clays may also be termed organophilic. In one or more embodiments,
the mineral clay mixtures comprises: a mineral clay (a) comprising 50 to 95 wt. %, based
on the weight of the mineral clay mixture, or 60 to 95 wt. %, or 70 to 90 wt. % of a
mineral clay selected from the group including sepiolite, palygorskite and mixtures of
sepiolite and palygorskite; and a mineral clay (b) comprising the balance by weight of the
mineral clay mixture, of a smectite. In one or more embodiments, the smectite may be a
natural or synthetic clay mineral selected from the group including hectorite,
montmorillonite, bentonite, beidellite, saponite, stevensite and mixtures thereof. The
Garamite line of products available from BYK Additives, (Gonzalez, TX) are
representative examples of mixed mineral clay products.

[0015] Both sepiolite and palygorskite are included in the broad grouping of
phyllosilicates, or sheet silicates, because they contain a continuous two-dimensional
tetrahedral sheet of composition T₃O₅ (T=Si, Al, Be, . . .) but they differ from other layer
silicates in lacking continuous octahedral sheets. Thus, they may have properties that differ from other layer silicates and the mineral clay mixture described above may also have differing properties as a result of their presence in the admixture. For example, when compared on a mass basis, the same mass of the mineral clay mixture may have a larger bulk volume than conventional suspending agents that use only smectite type layer silicates. As a result of the increased bulk volume, when using the mineral clay mixture it may be possible to use less suspending agent than is conventionally used to achieve the fluid properties to suspend hydratable polymer therein. The use of less suspending agent may also facilitate easier mixing of the mineral clay mixture into the carrier fluid.

[0016] In one or more embodiments, the alkyl quaternary ammonium salts employed for treating the mineral clay mixtures comprise alkyl quaternary ammonium salts containing the same or different straight and/or branched-chain saturated and/or unsaturated alkyl groups of 1 to 22 carbon atoms and the salt moiety is selected from the group including chloride, bromide, methylsulfate, nitrate, hydroxide, acetate, phosphate and mixtures thereof. In one or more embodiments, the alkyl quaternary ammonium salts are dimethyl di(hydrogenated tallow) ammonium chloride, methylbenzyl di(hydrogenated tallow) ammonium chloride, dimethylbenzyl hydrogenated tallow ammonium chloride, dimethyl hydrogenated tallow-2 ethylhexylammonium methylsulfate and mixtures of two or more of the above.

[0017] Examples of other organophilic clays include Tixogel®, a product available from United Catalyst Inc. (Louisville, KY), Bentone®, a product available from Rheox Company (Hightestown, NJ), and Claytone®, a product available from BYK Additives (Gonzalez, TX).

[0018] In one or more embodiments, the suspending agent may be included in the water-free slurry in an amount ranging from about 0.1% to 10% by weight of the water-free slurry, or from about 0.25% to 8% by weight of the water-free slurry, or from about 0.35% to 6% by weight of the water free slurry, or from about 0.5% to 4% by weight of the water free slurry.
In one or more embodiments, a water-free hydratable polymer slurry may include a polymeric suspension stabilizer. In one or more embodiments, the polymeric suspension stabilizer may be selected from polysaccharides including diutan gum, xanthan gum, dextran, welan gum, gellan gum, pullulan, hydroxyethyl cellulose, hydroxypropyl cellulose, guar, and guar derivatives. The polymeric suspension stabilizer is a distinct and different component than the hydratable polymer. Thus, if a particular hydratable polymer is used in the water-free slurry then the polymeric suspension stabilizer will be a compound having a differing composition than the hydratable polymer. When water is encountered, the polymeric suspension stabilizer may keep the hydratable polymer suspended while polymer hydration is taking place. Whereas some polymeric suspension stabilizers may not perform as well at elevated temperatures, some polymeric suspension stabilizers, for example diutan gum, may be able to suspend hydratable polymers during their hydration at elevated temperatures. Further, the addition of a polymeric suspension stabilizer to a carrier fluid may provide the fluid with pseudoplastic properties. Fluids with pseudoplastic properties exhibit viscosity which increases and decreases virtually instantaneously in response to the removal and application of shear, respectively. Thus, a pseudoplastic fluid may readily flow, while also being capable of suspending or stabilizing solid components therein.

In one or more embodiments, the polymeric suspension stabilizer may be included in the water-free slurry in an amount ranging from about 0.5% to 10% by weight of the water-free slurry, or from about 0.75% to 8% by weight of the water-free slurry, or from about 1.5% to 6% by weight of the water-free slurry.

A carrier fluid or solvent base fluid for forming the hydratable polymer slurry according to the present disclosure can generally be any fluid that will suspend a dispersion of the suspension agent and the hydratable polymer to form a suspension in which the polymer is not soluble and where the suspension has a relatively high polymer concentration but a viscosity low enough to be pumpable under oilfield service conditions. The carrier fluid also should not hydrate the polymer being suspended. The polymer should not be readily soluble in the solvent or the concentrated suspension may become too viscous or may form a liquid or a solid. The carrier fluid base can be
selected from one of three groups of compounds. In one or more embodiments a first group may include low viscosity, low-volatility mutual solvents and mixtures thereof. The term “mutual solvent” is meant to indicate a solvent that can dissolve in substantial amounts both hydrophilic and lipophilic substances, in other words, a mutual solvent according to the present disclosure is miscible with water-based and oil-based fluids. Mutual solvents may include by way of non-limiting examples various alcohols including 2-butoxyethanol, glycols and glycol ethers such as: ethylene glycol monobutyl ether (EGMBE) (available from The Dow Chemical Company, Midland, Mich., under the trade name Dowanol® EB), hexylene glycol, 2-methyl hexanol, propylene glycol n-butyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, dipropylene glycol methyl ether (available from The Dow Chemical Company, Midland, Mich., under the trade name Dowanol® DPM), dipropylene glycol n-butyl ether (available from The Dow Chemical Company, Midland, Mich., under the trade name Dowanol® DPNB), diethylene glycol ethyl ether, propylene glycol, diethylene glycol methyl ether, and the like. In one or more embodiments, mutual solvents may be used in combination with a hydrocarbon solvent such as mineral oil, however, in other embodiments mutual solvents may be used without a hydrocarbon solvent. Not all mutual solvents are suitable; excluded are those that are too viscous or that form polymer suspensions that are too viscous under normal operating conditions. Specifically, it is highly desirable to have one formulation that can be used under a variety of conditions, and very undesirable to have a formulation that cannot be used under certain conditions. For example, larger polyethylene glycols (PEG’s), even relatively low molecular weight materials such as PEG 200 or PEG 400 are not suitable because they are too viscous and/or form suspensions that have viscosities that are too high. Suitable mutual solvents have at least one of a molecular weight less than about 200; a freezing points lower than about -75 °C, and viscosities less than about 5 cP at 25 °C.

[0022] In one or more embodiments, a second group of compounds from which the carrier fluid may be selected comprises any of the mono alkyl esters of long chain fatty acids, derived from vegetable oils or animal fats that are commonly termed “biodiesel”. These are known materials in the fuels and engine industries, as fuels for compression-
ignition (diesel) engines. The pure materials are known as “B100” biodiesel. Mixtures with conventional petroleum diesel fuels are known as “Bxyz” biodiesel, where xyz is the percent biodiesel in the fuel. B100 may be useful in the present application. Biodiesel is made by reacting the vegetable oils and/or animal fats with an alcohol; methanol is the usual choice but other alcohols may be used. Biodiesel is non-toxic and biodegradable. Biodiesel is available from many sources, including Biodiesel Industries, Marathon, Fla.; Stepan Company, Northfield, Ill.; and West Central Soy, Ralston, Iowa. Biodiesel is formulated for its burning characteristics, and certain physical properties such as pour point, volatility and boiling point. Its characteristics as a solvent and its miscibility with other materials are not a factor in its manufacture.

[0023] In one or more embodiments, a third group of compounds from which the carrier fluid may be selected comprises hydrocarbon fluids, including aliphatic hydrocarbons, diesel, and the like. In some embodiments, aromatic groups in the carrier fluid may be avoided in carrier fluids and/or are only present in low amounts since aromatic groups can influence the gelling process of a hydrated polymer. In one or more embodiments, the aliphatic hydrocarbon is used in mixture with the mutual solvents containing pendent hydroxyl functional groups. Suitable examples of aliphatic hydrocarbons include, but are not limited to: cyclohexane; Exxsol® solvents commercially available from ExxonMobil including Exxsol® D40, D60, D80, D110, and the like; heptane; hexane; lactane; low-aromatic base oil; mineral oil; white mineral oil; mineral seal oil; mineral spirits; VM & P naphtha; kerosene; hydrotreated kerosene; diesel; middle distillate fuels; isoparaffinic and naphthenic aliphatic hydrocarbon solvents; dimers and higher oligomers of propylene; butane; hydrotreated light petroleum distillates; and the like. Particularly useful may be a naphthenic type hydrocarbon solvent having a boiling point range of about 91.1 °C-113.9 °C (196°F-227 °F) sold as “Exxsol® D80” by ExxonMobil, Houston, Tex. While any functional amount of aliphatic hydrocarbon may be incorporated into the suspension, in some embodiments the amount of aliphatic hydrocarbon is up to about 25% by weight based on total suspension weight, or about 5% to about 20% by weight based on total suspension weight, or about 7% to about 17% by weight based on total suspension weight.
[0024] It is to be understood that in one or more embodiments, the carrier fluid can be a mixture of mutual solvents, a mixture of biodiesels, or a mixture of the two, including mixtures of mixtures. The mutual solvents and biodiesel of the present disclosure are much more environmentally friendly than diesel.

[0025] In one or more embodiments, the carrier fluid may be included in the water-free slurry in an amount from about 30% to 90% by weight of the water-free slurry, or from about 35% to 80% by weight of the water-free slurry, or from about 40% to 70% by weight of the water-free slurry, or from about 45% to 60% by weight of the water-free slurry.

[0026] In one or more embodiments, the components of the water-free slurry described above may be mixed together by any method known in the art to form a homogenous slurry. In one or more embodiments, a method of treating a subterranean formation that utilizes a water-free slurry of the present disclosure may include mixing an aqueous fluid with a water-free slurry of the present disclosure to create a mixed fluid and then circulating the mixed fluid through a wellbore penetrating the subterranean formation. The aqueous fluid may be selected from fresh water, produced water, brines, sea water, and the like. In one or more embodiments, the mixed fluid may contain the hydratable polymer in an amount from about 4% to 7% by weight of the mixed fluid. In one or more embodiments, the volume ratio of aqueous fluid to water-free slurry in a mixed fluid is between about 1 and 15, or between about 2 and 12, or between about 4 and 10.

[0027] In one or more embodiments, circulating the mixed fluid through the wellbore may be followed by circulating a fluid containing a crosslinking agent therein, with the crosslinking agent being circulated to crosslink the hydratable polymer that was previously circulated as part of the mixed fluid. In one or more embodiments, the crosslinking agent is circulated after circulating the mixed fluid in order to give the hydratable polymer sufficient time to hydrate within the mixed fluid prior to it being contacted with the crosslinking agent. Appropriate crosslinking agents for polyacrylamide polymers and copolymers may include chromic acetate, multivalent metal ion containing compounds or complexes, polyethyleneimine,
hexamethylenetetramine (HETA), glyoxal, paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, 1,3,5-trioxane, and terephthaldehyde and the like. In one or more embodiments, the multivalent metal ions that may be used as solid crosslinking agents for the hydratable polymer may include chromium-based, zirconium-based, aluminum-based, and titanium-based compounds and complexes. In more specific embodiments, a zirconium ion complex may be zirconium ion complexed by a hydroxyalkylated ethylene diamine ligand, such as N,N,N',N'-tetrakis-(2-hydroxypropyl)ethylenediamine and N,N,N',N'-tetrakis-(hydroxyethyl)ethylenediamine. Further, the zirconium ion complex may include those disclosed in U.S. Patent No. 8,252,731 and U.S. Patent No. 8,236,739.

[0028] Skilled artisans will appreciate that the specific crosslinking agent chosen may depend on the specific hydratable polymer chosen for the water-free slurry and the particular application or purpose for circulating the water-free slurry downhole. Therefore, the crosslinking agent is not particularly limited and may be any species known to crosslink the hydratable polymers included in this disclosure.

[0029] EXAMPLES

[0030] Example 1 – Slurry Stability at Room Temperature

[0031] Eight water-free slurries were formed using a single carrier fluid, a suspending agent, and a hydratable polymer. Table 1 shows the components and their amounts in each fluid. The mineral oil used was Escaid™-110, available from ExxonMobil Chemical. In this example, the conventional organophilic clay used as a suspending agent was alkyl quaternary ammonium montmorillonite. The mineral clay mixture used as the suspending agent is Garamite 1958, available from BYK Additives & Instruments. The hydratable polymer used was Alcoflood® 254S, a granular solid polyacrylamide available from BASF. In Table 1, EGMBE refers to the mutual solvent ethylene glycol monobutyl ether.

<table>
<thead>
<tr>
<th>Components</th>
<th>% (wt/wt)</th>
</tr>
</thead>
</table>

10
<table>
<thead>
<tr>
<th>Slurry #</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
<th>(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Oil</td>
<td>48</td>
<td>-</td>
<td>47.3</td>
<td>-</td>
<td>48</td>
<td>-</td>
<td>47.3</td>
<td>-</td>
</tr>
<tr>
<td>EGMBE</td>
<td>-</td>
<td>48</td>
<td>-</td>
<td>47.3</td>
<td>-</td>
<td>48</td>
<td>-</td>
<td>47.3</td>
</tr>
<tr>
<td>Conventional</td>
<td>2.0</td>
<td>2.0</td>
<td>2.7</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Organophilic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral Clay</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydratable</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

[0032] The slurry stability was tested by placing a specific volume of slurry in a graduated cylinder and allowing the slurries to age, un-agitated, at room temperature while recording the volume percent of free fluid observed over time. The results of this test are shown in Table 2 below. In the table a dash means that no measurement was taken for that particular time slot.

<table>
<thead>
<tr>
<th>Time</th>
<th>Slurry Stability (volume % free fluid observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slurry #</td>
</tr>
<tr>
<td>3 hrs</td>
<td></td>
</tr>
<tr>
<td>12 hrs</td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td></td>
</tr>
<tr>
<td>3 days</td>
<td></td>
</tr>
<tr>
<td>5 days</td>
<td></td>
</tr>
<tr>
<td>1 week</td>
<td></td>
</tr>
</tbody>
</table>
Example 2 – Hydration of Water-Free Slurry

In this example three slurries from the table above were tested for their hydration performance upon mixing with water and their phase state after mixing.

Slurry 3 was added to water and agitated for 1 hour during the hydration stage of the test. After agitation ceased, phase separation occurred within 5 hours.

Slurry 7 was added to water and agitated for 1 hour during the hydration stage of the test. After being mixed with water and ceasing the agitation, the mixture was stable showing only a 2 vol. % phase separation over 2 days, and an 8 vol. % phase separation over 15 days, with the mixture becoming homogenous quickly after re-mixing via agitation.

Slurry 8 was added to water and agitated for 1 hour during the hydration stage of the test. After agitation ceased, phase separation occurred within 5 hours.

Example 3 – Addition of Polymeric Suspension Stabilizer

In this example, four slurries were prepared utilizing Alcoflood® 254S, the granular solid polyacrylamide available from BASF, mixed into mineral oil (USP 138) or a EGMBE mutual solvent. The mineral clay mixture used as the suspending agent is Garamite 1958, available from BYK Additives & Instruments. The diutan gum is the polymeric suspension stabilizer. Table 3 below shows the details of the composition of each slurry.

<table>
<thead>
<tr>
<th>Components</th>
<th>% (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry # (12)</td>
<td>(13)</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>47.7</td>
</tr>
<tr>
<td>EGMBE</td>
<td>-</td>
</tr>
<tr>
<td>Mineral Clay Mixture</td>
<td>2.3</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Hydratable Polymer</td>
<td>50</td>
</tr>
<tr>
<td>Diutan Gum</td>
<td>-</td>
</tr>
</tbody>
</table>

[0040] Each of these slurries was then hydrated by being mixed with an equivalent volume of fresh water and agitated for a period of time before ceasing agitation to determine if phase separation would occur. Slurries that did not include the diutan gum as a polymeric suspension stabilizer exhibited phase separation after mixing with fresh water and hydrating at room temperature, while slurries that did include the diutan gum as a polymeric suspension stabilizer did not exhibit phase separation after mixing with fresh water and hydrating at room temperature. Additionally, slurries 12 and 13 were tested in a similar manner at elevated temperature (180 °F) and slurry 12 exhibited phase separation, while slurry 13 (containing diutan) did not exhibit phase separation.

[0041] A linear gel prepared with a slurry similar in composition to slurry 13 above (with diutan), was foamed via high shear mixing achieving a high foam quality (65%). Additionally, the foamed sample aged unagitated at room temperature remained stable, showing no settling or defoaming, for 24 hours indicating its stability.

[0042] A linear gel prepared with a slurry similar in composition to slurry 15 above (with diutan) was foamed via high shear mixing. This sample, when aged unagitated at room temperature of 180 °F, also showed no settling or defoaming for 24 hours indicating its stability. However, a linear gel prepared with a slurry similar in composition to slurry 14 above (without diutan), was foamed via high shear mixing but phase separation occurred within 5 hours of removing the agitation.

[0043] Example 4 – Water control system with polymeric gel cross-linking

[0044] In this test, dry hydratable polymer or a water-free slurry containing the same hydratable polymer were mixed with tap water to achieve a concentration of hydratable polymer of 5% by weight of the mixed fluid. The hydratable polymer used in all samples
was Alcoflood® 254S, the granular solid polyacrylamide available from BASF. After a hydration period where the mixed fluid is agitated, phenyl acetate (4% by weight of mixed fluid) and hexamethylenetetramine (2% by weight of the mixed fluid) are added to the mixed fluid to initiate crosslinking. The fluid is then loaded in a rheometer preheated to 212 °F and the viscosity is measured over time at 100 l/s shear. The results of this test are shown in FIG. 1.

[0045] In another test, either dry hydratable polymer or a water-free slurry containing the same hydratable polymer were mixed with tap water to achieve a concentration of hydratable polymer of 5.25% by weight of the mixed fluid. The hydratable polymer used in all samples was Alcoflood® 254S, the granular solid polyacrylamide available from BASF. After a hydration period where the mixed fluid is agitated, sodium lactate (1.3% by weight of mixed fluid) chromic acetate (1.07% by weight of the mixed fluid), and an amphoteric surfactant (1.5% by weight of the mixed fluid) are added to the mixed fluid to initiate crosslinking. The mixed fluid is then foamed and loaded in a rheometer preheated to 145 °F and the viscosity is measured over time at 100 l/s shear. The results of this test are shown in FIG. 2.

[0046] Example 5

[0047] In this example multiple slurries of hydratable polymer, polymeric suspension stabilizer, and suspending agent in a variety of carrier fluids were formed. The carrier fluids used were multiple mineral oils, EGBME, and diesel. The hydratable polymer was Alcoflood® 254S, the granular solid polyacrylamide available from BASF. The mineral clay mixture used as the suspending agent is Garamite 1958, available from BYK Additives & Instruments. The diutan gum is the polymeric suspension stabilizer. Table 4 below shows the details of the composition of each slurry.

<table>
<thead>
<tr>
<th>Components</th>
<th>% (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry #</td>
<td>(16)</td>
</tr>
<tr>
<td></td>
<td>(17)</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
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<td></td>
<td>(21)</td>
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<td></td>
<td>(22)</td>
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<tr>
<td>Mineral Oil</td>
<td>46.54</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>Mineral Oil (Alveg)</td>
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</tr>
<tr>
<td>Mineral Oil (P&amp;W)</td>
<td>46.54</td>
</tr>
<tr>
<td>Mineral Oil (Escald 110)</td>
<td>45.94</td>
</tr>
<tr>
<td>EGMBE</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
</tr>
<tr>
<td>Mineral Clay Mixture</td>
<td>0.6</td>
</tr>
<tr>
<td>Hydratable Polymer</td>
<td>50</td>
</tr>
<tr>
<td>Polymeric Suspension Stabilizer</td>
<td>2.86</td>
</tr>
</tbody>
</table>

[0048] The slurry stability was tested by placing a specific volume of slurry in a graduated cylinder and allowing the slurries to age, un-agitated, at room temperature while recording the volume percent of free fluid observed over time. The results of this test are shown in Table 5 below. In this table, the dashed lines indicate measurements that were not taken at that time slot, while “traces” indicates that the separation % is small enough to not be measurable.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Slurry Stability (volume % free fluid observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry #</td>
<td>(16) (17) (18) (19) (20) (21) (22)</td>
</tr>
</tbody>
</table>

15
<table>
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<tr>
<th></th>
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<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>traces</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>traces</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>traces</td>
<td>2</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>traces</td>
<td>2</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>traces</td>
<td>2</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.
CLAIMS

What is claimed:

1. A water-free slurry, comprising:
   a non-aqueous carrier fluid;
   a suspension agent comprising a mineral clay mixture; and
   hydratable polymer microbeads.

2. The water-free slurry of claim 1, wherein a majority of the hydratable polymer microbeads have a diameter greater than about 100 microns.

3. The water-free slurry of claim 1, further comprising a polymeric suspension stabilizer selected from at least one of diutan gum, xanthan gum, dextran, welan gum, gellan gum, pullulan, hydroxyethyl cellulose, hydroxypropyl cellulose, guar, and guar derivatives.

4. The water-free slurry of claim 3, wherein the polymeric suspension stabilizer is present in the slurry in an amount ranging from about 0.5% to 10% by weight of the slurry.

5. The water-free slurry of claim 1, wherein the non-aqueous carrier fluid is at least one of a mutual solvent, mono alkyl esters of long chain fatty acids, and hydrocarbon fluids.

6. The water-free slurry of claim 1, wherein the non-aqueous carrier fluid is present in the slurry in an amount ranging from about 30% to 90% by weight of the slurry.

7. The water-free slurry of claim 1, wherein the mineral clay mixture comprises:
   a mineral clay (a) comprising 50 to 95 wt. %, based on the weight of the mineral clay mixture, of a mineral clay selected from the group including sepiolite, palygorskite and mixtures of sepiolite and palygorskite; and
   a mineral clay (b) comprising the balance by weight of the mineral clay mixture, of a smectite.

8. The water-free slurry of claim 1, wherein the suspension agent is present in the slurry in an amount ranging from about 0.1% to 10% by weight of the slurry.
9. The water-free slurry of claim 1, wherein the hydratable polymer is selected from polyacrylamide and acrylamide copolymers thereof, guar, hydroxypropyl guar (HPG), hydrophobically modified hydroxypropyl guar (HMHPG), carboxymethyl guar (CMG), carboxymethyl hydroxypropyl guar (CMHPG); carboxymethyl hydroxyethyl cellulose (CMHEC), carboxymethylcellulose, other cellulosics and cellulosic derivatives such as hydroxyethylcellulose and hydroxypropylcellulose; xanthan gum, modified starches, glucomannan gums, succinoglycan, scleroglycan, o-carboxychitosans, polyvinylsaccharides, and heteropolysaccharides.

10. The water-free slurry of claim 1, wherein the hydratable polymer is present in the slurry in an amount ranging from about 5% to 70% by weight of the slurry.

11. The water-free slurry of claim 1, wherein the hydratable polymer microbeads have a \( d_{10} \) of at least 150 microns.

12. The water-free slurry of claim 1, wherein the mineral clay mixture has been treated by alkyl quaternary ammonium salts containing the same or different straight and/or branched-chain saturated and/or unsaturated alkyl groups of 1 to 22 carbon atoms; and wherein the salt moiety is selected from the group including chloride, bromide, methylsulfate, nitrate, hydroxide, acetate, phosphate and mixtures thereof.

13. A method of treating a subterranean formation, comprising:
   mixing an aqueous fluid with a water-free slurry to create a mixed fluid, the water-free slurry comprising:
   a non-aqueous carrier fluid;
   a suspension agent comprising a mineral clay mixture; and
   hydratable polymer microbeads; and
   circulating the mixed fluid through a wellbore penetrating the subterranean formation.

14. The method of claim 13, further comprising circulating a fluid including a crosslinking agent through the wellbore penetrating the subterranean formation.
15. The method of claim 13, wherein the volume ratio of aqueous fluid to water-free slurry in the mixed fluid is between about 1 and 15.

16. The method of claim 13, wherein the water free slurry further comprises a polymeric suspension stabilizer selected from at least one of diutane gum, xanthan gum, dextran, welan gum, gellan gum, pullulan, hydroxyethyl cellulose, hydroxypropyl cellulose, guar, and guar derivatives.

17. The method of claim 13, wherein the non-aqueous carrier fluid is at least one of a mutual solvent, mono alkyl esters of long chain fatty acids, and hydrocarbon fluids.

18. The method of claim 13, wherein the mineral clay mixture comprises:
   a mineral clay (a) comprising 50 to 95 wt. %, based on the weight of the mineral clay mixture, of a mineral clay selected from the group including sepiolite, palygorskite and mixtures of sepiolite and palygorskite; and
   a mineral clay (b) comprising the balance by weight of the mineral clay mixture, of a smectite.

19. The method of claim 13, wherein the hydratable polymer is selected from polyacrylamide and acrylamide copolymers thereof, guar, hydroxypropyl guar (HPG), hydrophobically modified hydroxypropyl guar (HMHPG), carboxymethyl guar (CMG), carboxymethyl hydroxypropyl guar (CMHPG), carboxymethyl hydroxyethyl cellulose (CMHEC), carboxymethylcellulose, other cellulosics and cellulosic derivatives such as hydroxyethylcellulose and hydroxypropylcellulose; xanthan gum, modified starches, glucomannan gums, succinoglycan, scleroglycan, o-carboxychitosans, polyvinylsaccharides, and heteropolysaccharides.

20. The method of claim 13, wherein a majority of the hydratable polymer microbeads have a diameter greater than about 100 microns.
Crosslinked Synthetic Polymer Gel
Tap Water + 5% Polyacrylamide + 4% Phenyl Acetate + 2% Hexamethylenetetraamine

FIG. 1
Rheology of Foamed Crosslinked Gel
Tap Water + 5.25% Polyacrylamide + 1.3% Sodium Lactate 60% Solution + 1.07% Chromic Acetate 50% Solution + 1.5% Amphoteric Surfactant 32.6% Solution

FIG. 2
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
   IPC(8) - C09K 8/00; C09K 8/60 (2016.01)
   CPC - C09K 8/05; C09K 8/032; C09K 8/16
According to International Patent Classification (IPC) or to both national classification and IPC

R FIFI HAS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
CPC - C09K 8/05; C09K 8/032; C09K 8/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - C09K 8/05; C09K 8/032; C09K 8/16; IPC(8) - C09K 8/00; C09K 8/60 (2016.01); USPC - 507/140,214

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(USPT,PGP,EPAB,JPAB); PatBase; Google Scholar. Search Terms: water-free non-aqueous suspension slurry
subterranean hydratable polymer carrier fluid clay cross-linker microbead particle stabilizer gum cellulose guar pullulan dextran sepiolite
pyogorskite smectite quaternary ammonium carbon atoms chain length

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>US 2006/026347 A1 (LIN et al.) 07 December 2006 (07.12.2006), paras [0010], [0023], [0031], [0052], [0053], [0057]; claims 1, 16</td>
<td>1-20</td>
</tr>
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</table>

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

* 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 mean
  "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: 01 October 2016

Date of mailing of the international search report: 07 NOV 2016

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Authorized officer:
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PCT Helpdesk: 571-272-4300
PCT ODP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)