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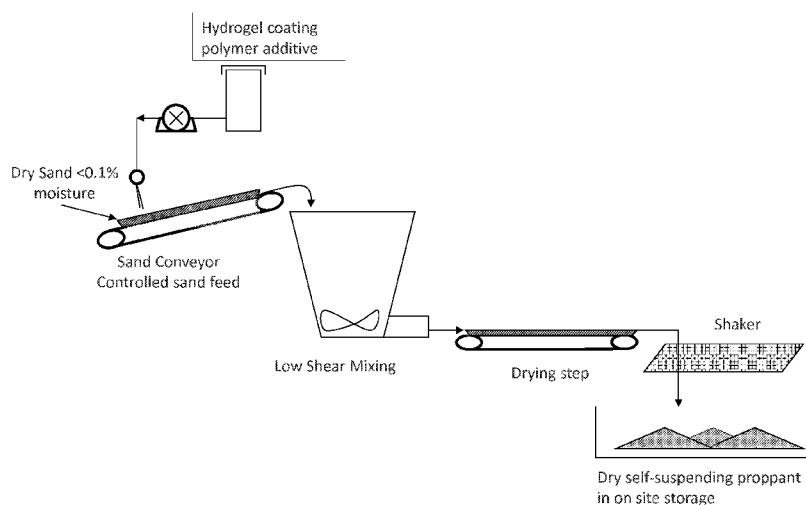


FIG. 1

(57) Abstract: The invention encompasses a modified proppant comprising a proppant particle and a hydrogel coating, wherein the hydrogel coating localizes on the surface of the proppant particle to produce the modified proppant. The invention also encompasses formulations comprising the modified proppant as well as methods for the manufacture and methods for the use of the modified proppant.



SELF-SUSPENDING PROPPANTS FOR HYDRAULIC FRACTURING

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 61/635,612, filed April 19, 2012, U.S. Provisional Application Serial No. 61/662,681, filed June 21, 2012, U.S. Provisional Application Serial No. 61/725,751, filed November 13, 2012 and U.S. Provisional Application Serial No. 61/764,792, filed February 14, 2013. The entire contents of the above-referenced applications are incorporated by reference herein.

FIELD OF APPLICATION

[0002] This application relates generally to systems and methods for fracturing technologies.

BACKGROUND

[0003] In the process of acquiring oil and/or gas from a well, it is often necessary to stimulate the flow of hydrocarbons via hydraulic fracturing. The term “fracturing” refers to the method of pumping a fluid into a well until the pressure increases to a level that is sufficient to fracture the subterranean geological formations containing the entrapped materials. This process results in cracks and breaks that disrupt the underlying layer to allow the hydrocarbon product to be carried to the well bore at a significantly higher rate. Unless the pressure is maintained, however, the newly formed openings close. In order to open a path and maintain it, a propping agent or “proppant” is injected along with the hydraulic fluid to create the support needed to preserve the opening. As the fissure is formed, the proppants are delivered in a slurry where, upon release of the hydraulic pressure, the proppants form a pack or a prop that serves to hold open the fractures.

[0004] To accomplish the placement of the proppants inside the fracture, these particles are suspended in a fluid that is then pumped to its subterranean destination. To prevent the particles from settling, a high viscosity fluid is often required to suspend them. The viscosity of the fluid is typically managed by addition of synthetic or naturally-based polymers. There are three common types of polymer-enhanced fluid systems in general use for suspending and transporting proppants during hydraulic fracturing operations: slickwater, linear gel, and crosslinked gel.

[0005] In slickwater systems, an anionic or cationic polyacrylamide is typically added as a friction reducer additive, allowing maximum fluid flow with a minimum of pumping energy. Since the pumping energy requirements of hydraulic fracturing are high, on the order of 10,000 to 100,000 horsepower, a friction reducer is added to slickwater fluids to enable high pumping rates while avoiding the need for even higher pumping energy.

While these polymers are effective as friction reducers, they are not highly effective as viscosifiers and suspending agents. Slickwater polymer solutions typically contain 0.5 to 2.0 gallons of friction reducer polymer per 1000 gallons of slickwater fluid, and the solutions have low viscosity, typically on the order of 3 to 15 cps. At this low viscosity, suspended proppant particles can readily settle out of suspension as soon as turbulent flow is stopped. For this reason, slickwater fluids are used in the fracturing stages that have either no proppant, proppant with small particle size, or low proppant loadings.

[0006] The second type of polymer enhanced fluid system is known as a linear gel system. Linear gel systems typically contain carbohydrate polymers such as guar, hydroxyethylcellulose, hydroxyethyl guar, hydroxypropyl guar, and hydroxypropylcellulose. These linear gel polymers are commonly added at a use rate of 10 to 50 pounds of polymer per 1000 gallons of linear gel fluid. These concentrations of linear gel polymer result in a fluid with improved proppant suspending characteristics vs. the slickwater fluid. The linear gel fluids are used to transport proppants, at loading levels of about 0.1 to 1 pound of proppant per gallon of fluid. Above this proppant loading level, a more viscous solution is typically required to make a stable suspension.

[0007] Crosslinked gel is the most viscous type of polymer-enhanced fluid used for transporting of proppant. In crosslinked gel systems, the linear gel fluid as described above is crosslinked with added reagents such as borate, zirconate, and titanate in the presence of alkali. Upon crosslinking of the linear gel fluid into a crosslinked gel fluid, the viscosity is much higher and the proppants can be effectively suspended. The linear gel and crosslinked gel fluids have certain advantages but they require a high dose rate of expensive polymer.

[0008] Modifications of proppant particles could be used advantageously to improve their performance in hydraulic fracturing systems. First, if the proppant particles were more buoyant, a less viscous suspension fluid could be used, which would still convey the particles to the target area but which would be easier to pump into the formation. Second, it is desirable that the proppants remain where they are placed throughout the lifetime of the well after they have been injected into a fracture line. If changes within the reservoir

during well production force the proppants out of position, production equipment can be damaged, and the conductivity of the reservoir formation can be decreased as the reservoir pores are plugged by the displaced proppants. Third, the proppants in the system should be resistant to closure stress once they are placed in the fracture. Closure stresses can range from 1700 psi in certain shale gas wells, up to and exceeding 15,000 psi for deep, high temperature wells. Care must be taken that the proppants do not fail under this stress, lest they be crushed into fine particles that can migrate to undesirable locations within the well, thereby affecting production. Desirably, a proppant should resist diagenesis during fracture treatment. The high pressures and temperatures combine with the chemicals used in frac fluids can adversely affect the proppant particles, resulting in their diagenesis, which can eventually produce fine particulate matter that can scale out and decrease the productivity of the well over time.

[0009] Current proppant systems and polymer-enhanced fracturing fluids endeavor to address these concerns, so that the proppants can be carried by the fracturing fluids, can remain in place once they arrive at their target destination, and can resist the closure stresses in the formation. One approach to preparing suitable proppants includes coating the proppant materials with resins. A resin-coated proppant can be either fully cured or partially cured. The fully cured resin can provide crush resistance to the proppant substrate by helping to distribute stresses among the grain particles. A fully cured resin can furthermore help reduce fine migration by encapsulating the proppant particle. If initially partially cured, the resin may become fully cured once it is placed inside the fracture. This approach can yield the same benefits as the use of a resin that is fully-cured initially. Resins, though, can decrease the conductivity and permeability of the fracture, even as the proppants are holding it open. Also, resins can fail, so that their advantages are lost. Resin-based systems tend to be expensive and they are still prone to settling out of suspension.

[0010] In addition, there are health, safety and environmental concerns associated with the handling and processing of proppants. For example, fine particulates (“fines”), such as crystalline silica dust, are commonly found in naturally occurring sand deposits. These fines can be released as a respirable dust during the handling and processing of proppant sand. With chronic exposure, this dust can be harmful to workers, resulting in various inhalation-associated conditions such as silicosis, chronic obstructive pulmonary disease, lung cancers, and the like. In addition to these health effects, the fines can cause “nuisance dust” problems such as fouling of equipment and contamination of the environment.

[0011] Another approach to preparing suitable proppants involves mixing additives with the proppant itself, such as fibers, elastomeric particles, and the like. The additives, though, can affect the rheological properties of the transport slurry, making it more difficult to deliver the proppants to the desired locations within the fracture. In addition, the use of additives can interfere with uniform placement of the proppant mixture into the fracture site. While there are known methods in the art for addressing the limitations of proppant systems, certain problems remain. There is thus a need in the art for improved proppant systems that allow precise placement, preserve fracture conductivity after placement, protect well production efficiency and equipment life, simplify hydraulic fracturing operations, reduce environmental impact, and promote worker health and safety. It is further desirable that such improved systems be cost-effective.

SUMMARY

[0012] Disclosed herein are embodiments of a modified proppant, comprising a proppant particle and a hydrogel coating, wherein the hydrogel coating localizes on the surface of the proppant particle to produce the modified proppant. In embodiments, the proppant particle comprises sand or comprises a resin-coated substrate. In additional embodiments, the proppant particle comprises bauxite, sintered bauxite, ceramic, or lower density materials. In embodiments, the modified proppant further comprises an adhesion promoter, wherein the adhesion promoter affixes the hydrogel coating to the resin-coated substrate. In embodiments, the hydrogel coating comprises a water-swelling polymer. In embodiments, the hydrogel coating comprises a polymer selected from the group consisting of polyacrylamide, poly(acrylic acid), carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, carboxymethyl guar, carboxymethyl hydroxypropyl guar gum, hydrophobically associating swellable emulsion polymers, and latex polymers. In embodiments, the modified proppant further comprises a cationic/anionic polymer pair comprising a cationic polymer and a high molecular weight anionic polymer. In embodiments, the cationic polymer is selected from the group consisting of poly-DADMAC, LPEI, BPEI, chitosan, and cationic polyacrylamide. In embodiments, the modified proppant further comprises a crosslinking agent. The crosslinking agent can comprise a covalent crosslinker. The covalent crosslinker can comprise a functional group selected from the group consisting of an epoxide, an anhydride, an aldehyde, a diisocyanate, and a carbodiimide. The covalent crosslinker can be selected from the group consisting of polyethylene glycol, diglycidyl ether,

epichlorohydrin, maleic anhydride, formaldehyde, glyoxal, glutaraldehyde, toluene diisocyanate, and methylene diphenyl diisocyanate, and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide. In embodiments, the crosslinking agent comprises an organometallic compound. In embodiments, the modified proppant further comprises a hydrophobic layer, which can be selected from the group consisting of fatty acids, hydrogenated oils, vegetable oils, castor oil, waxes, polyethylene oxides, and polypropylene oxides. In embodiments, the modified proppant comprises a chemical breaker, for example, an oxidative breaker. In embodiments, the modified proppant further comprises a delayed hydration additive. The delayed hydration additive can be selected from the group consisting of a low hydrophilic-lipophilic balance surfactant, an exclusion agent capable of excluding a finishing surfactant, a light ionic crosslinking agent, a light covalent crosslinking agent and a monovalent salt charge shielder. In embodiments, the modified proppant further comprises an alcohol, which can be selected from the group consisting of ethylene glycol, propylene glycol, glycerol, propanol, and ethanol. In embodiments, the modified proppant further comprises an anticaking agent. In embodiments, the hydrogel coating comprises an additive, which can be a chemical additive. In embodiments, the additive is a tracer or a chemical breaker. In embodiments, the modified proppant contains less fines than a proppant particle that is not modified. In embodiments, the hydrogel coating comprises an additive, which can be a chemical additive or a tracer.

[0013] The invention additionally encompasses a hydraulic fracturing formulation comprising a modified proppant particle described herein.

[0014] Further disclosed herein are formulations that comprise the modified proppant as disclosed herein. Also disclosed herein are methods for fracturing a well, comprising preparing the hydraulic fracturing formulation as disclosed herein, and introducing the hydraulic fracturing formulation into the well in an effective volume and at an effective pressure for hydraulic fracturing, thereby fracturing the well.

[0015] Also disclosed herein are methods of manufacturing a modified proppant, comprising providing a proppant substrate particle and a fluid polymeric coating composition; applying the fluid polymeric coating composition on the proppant substrate particle; wherein the fluid polymeric coating composition comprises a hydrogel polymer, and wherein the hydrogel polymer localizes on the surface of the proppant substrate particle to produce the modified proppant. In embodiments the fluid polymeric coating comprises a crosslinking species. In embodiments, the method further comprises the step

of drying the modified proppant. In embodiments, the manufacturing takes place at or near a point of use for the modified proppant. In embodiments, the proppant substrate particle comprises sand, which can be obtained at or near the point of use for the modified proppant. In embodiments, the method further comprises a step of adding an alcohol
5 selected from the group consisting of ethylene glycol, propylene glycol, glycerol, propanol, and ethanol during or before the step of applying the fluid polymeric coating composition on the proppant substrate particle. In embodiments, the method further comprises a step of adding an inversion promoter during or following the step of mixing the proppant substrate particles and the fluid polymer coating composition. In
10 embodiments, the method further comprises the step of adding an anticaking agent to the modified proppant.

[0016] Further disclosed herein are methods of manufacturing a hydrogel-coated proppant, comprising providing a proppant substrate particle and a formulation comprising a coating precursor, wherein the coating precursor is capable of forming a
15 hydrogel coating on the proppant substrate particle by in situ polymerization; applying the formulation to the proppant substrate particle; and polymerizing the coating precursor in juxtaposition to the proppant substrate particle to form the hydrogel-coated proppant.

BRIEF DESCRIPTION OF THE FIGURES

[0017] FIG. 1 is a flow diagram of a manufacturing process for self-suspending
20 proppants.

[0018] FIG. 2 is a graph of Bed Height (mm) versus Shear Time (min) for SSP, SSP + Glycerol and SSP + Ethal.

[0019] FIG. 3 is a graph of Bed Height (mm) versus Shear Time (min) for samples with glycerol and without glycerol.

25 **[0020]** FIG. 4 is a graph of Bed Height (mm) versus Shear Time (min) for samples with glycerol and without glycerol.

DETAILED DESCRIPTION

1. Modified Proppant Particles

[0021] Disclosed herein are systems and methods for forming and using proppant
30 particles having a hydrogel surface layer to enhance the hydrodynamic volume of the proppant particles during fluid transport, creating a more stable proppant suspension that resists sedimentation, separation, and screenout before the proppant can reach the

intended target destination in the fracture. Further benefits of the hydrogel-coated proppants as disclosed herein include lower tendency to erode equipment, lower friction coefficient in the wet state, good bonding adhesion with each other after placement in a fracture site, resistance to uncontrolled fines formation, and anti-fouling properties attributable to the hydrophilic surface. In embodiments, the disclosed systems for forming proppant particles can be applied to the types of proppant substrates most widely used, e.g., sand and ceramics. In other embodiments, the proppant particles can be formed from a variety of substrates, including fibrous materials, as would be available to those having ordinary skill in the art. In certain embodiments, the proppant particles can be fabricated so that they resist crush or deformation, so that they resist displacement, and so that they can be suspended in less viscous fluid carriers for transporting into the formation.

[0022] In embodiments, these self-suspending proppants are formed by modification of a particulate substrate with a water swellable polymer coating such as a hydrogel. In embodiments, the particulate substrate can be modified with the polymer coating before the particulate substrate is introduced into the fracturing fluid. In embodiments, the amount of hydrogel polymer coating can be in the range of about 0.1 to about 10% based on the weight of the proppant. In embodiments, the hydrogel layer applied onto the surface of the proppant substrate can be a coating thickness of about 0.01% to about 20% of the average diameter of the proppant substrate. Upon hydration and swelling of the hydrogel layer in the fracturing fluid, the hydrogel layer can become expanded with water, such that the hydrogel layer thickness can become about 10% to about 1000% of the average diameter of the proppant substrate.

[0023] Methods for modification of proppant include spraying or saturation of a liquid polymer formulation onto a proppant substrate, followed by drying to remove water or other carrier fluids. The drying process can be accelerated by application of heat or vacuum, and by tumbling or agitation of the modified proppant during the drying process. The heating can be applied by forced hot air, convection, friction, conduction, combustion, exothermic reaction, microwave heating, or infrared radiation. Agitation during the proppant modification process has a further advantage of providing a more uniform coating on the proppant material.

[0024] FIG. 1 shows an example of a manufacturing process for the self-suspending proppant using dried sand and a liquid polymer. In the depicted embodiment, sand is conveyed into a mixing vessel, and a liquid polymer composition is sprayed via pump and

spray nozzles onto the sand along the conveyor belt. The sand and liquid polymer report to a low shear mixing vessel, where the ingredients are further blended. After mixing, the modified sand containing the liquid polymer is sent to a dryer to remove water and/or organic carrier fluids associated with the liquid polymer. After the drying step, the modified sand is passed through size classification equipment, such as a sieve, to remove over-sized agglomerates. Mechanical mixers, shear devices, grinders, or crushers can be used to break up aggregates to allow the material to pass through the appropriate sized sieve. The finished material is then stored for shipment or use.

[0025] In embodiments, the sand that is used to produce self-suspending proppant is pre-dried to a moisture content of <1%, and preferably <0.1% before being modified with a hydrogel polymer. In embodiments, the sand temperature at the time of mixing with the liquid polymer is in the range of about 10 to about 200° C, and preferably in the range of about 15 to about 60° C.

[0026] In embodiments, the sand is contacted with the liquid polymer composition by means of spraying or injecting. The amount of liquid polymer composition added is in the range of about 1 to about 20%, and preferably about 2 to about 10% by weight of the sand. The sand and liquid polymer are blended for a period of about 0.1 to about 10 minutes. In a preferred embodiment, the mixing equipment is a relatively low shear type of mixer, such as a tumbler, vertical cone screw blender, v-cone blender, double cone blender, or ribbon blender. In embodiments, the mixing equipment can be equipped with forced air, forced hot air, vacuum, external heating, or other means to cause evaporation of the carrier fluids.

[0027] In embodiments, the modified sand containing the liquid polymer is dried to remove water and/or organic carrier fluids associated with the liquid polymer. The dryer equipment can be a conveyor oven, microwave, or rotary kiln type. In an embodiment the drying step is carried out in such a way that the dried, modified sand contains less than 1% by weight of residual liquids, including water and any organic carrier fluids associated with the liquid polymer composition.

[0028] In embodiments, the same equipment can be used to blend the sand with the liquid polymer and to dry the blended product in a single processing stage, or in a continuous production line.

[0029] In other embodiments, methods for modification of proppant include synthesis of a hydrogel coating *in situ*, or in the presence of the proppant particle, resulting in a hydrogel layer encapsulating the surface of the proppant particle. As an example, the *in*

situ synthesis of the hydrogel can be accomplished by combining proppant particles with coating precursor monomers and/or macromonomers followed by a polymerization step. In other exemplary instances a water-soluble polymer can be dissolved in monomers, with or without solvent, followed by polymerization in the presence of the proppant particles, resulting in the formation of interpenetrating polymer networks as a coating on the proppants. In other exemplary instances, the water-soluble polymer is dispersed in the monomers, with or without solvent, and the subsequent polymerization will result in proppants encapsulated by a hydrogel consisting of water-soluble polymer particles locked up by the newly formed polymer. The monomers or macromonomers used can be selected from monomers that result in water-soluble polymers. In other exemplary instances, the particles can be encapsulated by non-water soluble polymer that will then be modified or hydrolyzed to yield the water-soluble hydrogel coating. As would be understood by those of ordinary skill in the art, the encapsulating layer can be formed by different polymerization techniques, with or without solvents. The *in situ* polymerization of polymer on the surface of proppant grains can have the advantage of reducing or eliminating drying steps.

[0030] By way of example, a water-soluble monomer(s) can be chosen from the following monomers or salts thereof: acrylic acid, methacrylic acid, acrylamide, methacrylamide, and their derivatives, carboxyethyl acrylate, hydroxyethylmethacrylate (HEMA), hydroxyethylacrylate (HEA), polyethyleneglycol acrylates (PEG-acrylates), N-isopropylacrylamide (NiPA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), sodium salt of styrene sulfonate, vinylsulphonic acid, (meth)allylsulphonic acid, vinylphosphonic acid, N-vinylacetamide, N-methyl-N-vinylacetamide, N-vinylformamide, N-methyl-N-vinylformamide, N-vinylpyrrolidone, N-butyrolactam or N-vinylcaprolactam, maleic anhydride, itaconic acid, vinyl acetate, dimethyldiallylammonium chloride; quaternized dimethylaminoethyl methacrylate (DMAEMA), (meth)acrylamidopropyltrimethylammonium chloride, methylvinylimidazolium chloride; 2-vinylpyridine; 4-vinylpyridine, and the like. The ratio of ionic to nonionic monomers can be selected to yield hydrogels with different charge density. In some instances, for example, it is desirable to have hydrogels with higher charge in order to yield coatings with faster hydration or swelling properties. In other instances the ionizable monomers can be selected to have higher or lower ionization constants to yield hydrogels more or less stable in brine environments. Other advantageous properties can be imparted by selection of appropriate charge densities.

[0031] In embodiments, coating precursors can include polyfunctional monomers that contain more than one polymerizable group and that will introduce the crosslinking or branching points in the hydrogel. Examples of these monomers are: pentaerythritol triallyl ether, PEG-diacrylates and methacrylates, N,N'-methylenebisacrylamide,
5 epichlorohydrin, divinyl sulfone, and glycidyl methacrylate. When such monomers are used, the crosslinking monomer will be in the range of about 0.001 to about 0.5 % of the total monomer content. In selecting a range for adding crosslinkers, one should be aware that adding excessive amounts of crosslinker could form brittle hydrogels that can fracture or degrade under pressure, and adding insufficient amounts of crosslinkers could
10 form hydrogels that can be easily detached from the surface particle under extreme conditions.

[0032] In embodiments, the monomers/macromonomers used are selected from coating precursor monomers that that will form a non-water soluble coating. After the coating is applied, its further modification will result in the water swellable polymer. As an
15 example, a polymeric coating containing hydrolysable groups can be formed, and subsequent hydrolysis will yield the hydrogel. Examples of monomers that fall in this category are esters, anhydrides, nitriles, and amides; for example the ester monomers methyl acrylate, t-butyl acrylate can be used. As another example, a monomer containing vinyl functionalities can form the hydrogel by different polymerization techniques with or
20 without solvents. The polymerization techniques include bulk, suspension, admicellar, solution polymerization.

[0033] In other embodiments, coating monomers or precursors can be selected to form a self-suspending proppant with a hydrogel comprising a polyurethane or polyurea. A list of suitable monomers to form polymers with polyurethane and/or polyurea functionalities
25 are: polyols such as ethylene glycol, propylene glycol, glycerin, trimethylolpropane, 1,2,6-hexanetriol, pentaerythritol, sorbitol, sucrose, α -methylglycoside, polyoxyalkylenes, such as PEG, copolymers of PEG-PPG, Pluronic, Tetronics, polyamines such as JEFFAMINE® polyetheramines. Among the isocyanates there may be mentioned toluene-diisocyanate, naphthalenediisocyanate, xylene-diisocyanate, tetramethylene
30 diisocyanate, hexamethylene diisocyanate, trimethylene diisocyanate, trimethyl hexamethylene diisocyanate, cyclohexyl-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate and the like. Other appropriate polymers can include HYPOL® hydrophilic polyurethane prepolymers from Dow, DESMODUR® and MONDUR® resins from Bayer (2,4'-diphenylmethanediisocyanate, 4,4'-diphenylmethanediisocyanate, and their mixtures),

and CONATHANE® (polyisocyanate functionalized prepolymers of toluene diisocyanate and poly(tetramethylene glycols)) from Cytec, and the like.

[0034] The coating of proppant particle with a polyurethane (PU) hydrogel can be carried out by conventional methods. In an embodiment, the coating can be performed in bulk without the use of solvents. For example, a typical formulation for a crosslinked PU hydrogel can be prepared in a one-step bulk polymerization process using a diisocyanate, polyoxyalkylene, and a multifunctional crosslinking agent. In an embodiment, the formulation will contain 10 to 80% of a polyoxyalkylene having the polyoxyalkylene molecular weight between 200 and 25,000.

[0035] Another method to form the hydrogel layer *in situ* can be carried out by dissolving or suspending a water-soluble polymer in a monomer formulation followed by polymerization of the monomer. The monomers can be selected from the previous list of water soluble monomers. In the case that the water-soluble polymer is dissolved in the monomer mixture, the resulting coating will consist in interpenetrating hydrogel network of the initial water-soluble polymer and the polymer formed *in situ*. In the case where the water-soluble polymer is suspended in the monomer mixture, the resulting coating will consist of a hydrogel coating in which the water soluble particles are locked up or entrapped. For example, these particles can be trapped inside the newly formed hydrogel coating or they can be bonded to the newly formed polymer. The water-soluble polymer can be dissolved or suspended in the monomer formulation in the presence or absence of a solvent and the polymerization can be carried out by different techniques.

[0036] Suitable water soluble polymers to be mixed with monomers can be selected from the group consisting of polyacrylamide, polyacrylic acid, copolymers of acrylamide with acrylic acid salts, polyethyleneglycol, polyvinylpyrrolidone, polyvinylalcohol, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, carboxymethyl guar, carboxymethyl hydroxypropyl guar gum, hydrophobically associating swellable emulsion polymers, starches, latex polymers, and the like.

[0037] Another method for modification of proppant particles includes grafting hydrophilic polymers onto the particle. The grafting of polymer chains onto the surface of the particle can be done by reactions such as Huisgen cycloaddition and other coupling or addition reactions that can immobilize the polymers onto the particle surface.

[0038] The proppant particle used for these purposes can be selected to have surface functional groups such as epoxy, vinyl, amine, hydroxyl, etc. Those groups can then react with polymers having groups capable of reacting with the functional groups on the

particle surface. For example, proppant particles comprising silica can be surface modified by silanes such as aminosilanes, vinylsilanes, epoxysilanes, and the like.

[0039] In embodiments, the polymers that will react with the functionalized particle are hydrophilic linear or branched polymers or copolymers. The polymer can have one or
5 more grafting moiety. In embodiments, the polymers can have functional groups such as amino, carboxyl or salts thereof, hydroxyl, thiol, acid anhydride, acid chloride and/or isocyanate groups which enable covalent binding to the functional groups of the particle. Examples of polymers that can be used to react with the functionalized particle are:
10 epoxide functionalized PEG, amine functionalized PEG, azide functionalized PEG, polyethyleneimine, polyacrylic acid, polyvinyl alcohol, and the like.

[0040] In embodiments the resulting hydrogel, in addition to having swellable properties, can have temperature responsive or pH-responsive properties. The resulting swellable properties of the proppant can thus be tuned. This is an added benefit for transporting proppant down the wellbore, since temperatures are lower at the early stages
15 in which proppant is transported and full swelling behavior is desirable; higher temperatures are expected inside the fractures where lower swelling of the hydrogel layer is desirable for packing improvement. The monomers used to make the temperature responsive hydrogel coated proppants can be selected from N-isopropylacrylamide (NiPA), ethylene oxide, propylene oxide, or macromonomers/polymers that display a
20 lower critical solution temperature (LCST).

[0041] In an embodiment, the process of converting a substrate such as sand into a self-suspending proppant can be conducted at or near the point of use, for example, at an oil or gas well site in preparation for hydraulic fracturing. This method has the advantage of converting a commodity material with high material handling costs, such as sand, into a
25 specialized material that has added features. The sand can be acquired from local sources or shipped directly from a sand mining site or warehouse, for modification at the point of use. This avoids having to ship sand first into a blending plant and then ship a second time from the blending plant to the point of use. In the case of sand, the shipping costs can be higher than the material costs, so avoidance of extra shipping is desirable for
30 controlling costs.

[0042] Hydrogel polymers that can be used to modify proppants in accordance with the systems and methods disclosed herein can be introduced, in embodiments, as oil-based emulsions, dispersions, water-based emulsions, latexes, solutions, and dispersions. In embodiments, the hydrogel polymer can be an alkali-swellable emulsion, wherein the

hydrogel properties of the polymer are not fully developed until the polymer is contacted with alkali. In this embodiment, the alkali-swellable emulsion can be coated onto the proppant substrate to form a modified proppant, and this modified proppant can be suspended in a fracturing fluid in the presence of an alkaline material.

5 [0043] In embodiments, an additive such as an alcohol selected from the group consisting of ethylene glycol, propylene glycol, glycerol, propanol, and ethanol can be added during or before the step of mixing the proppant substrate particles and the liquid polymer coating composition. In embodiments, inversion promoters useful as additives in the polymer coating formulations for self-suspending proppants can include high HLB
10 surfactants, such as polyethylene oxide lauryl alcohol surfactant, (ETHAL LA-12/80% from ETHOX), ethylene glycol, propylene glycol, water, sodium carbonate, sodium bicarbonate, ammonium chloride, urea, barium chloride, and mixtures thereof. In embodiments, inversion promoters can serve the function of facilitating the release of active polymer ingredients from the internal phase of an oil based emulsion polymer into
15 the (typically aqueous) process fluid to be treated. Since this process converts an oil continuous polymer into a water continuous environment, it can be characterized as a phase inversion.

[0044] In other embodiments, the proppant substrate can be modified with a polymer formulation, without the need for a drying step. This can be accomplished by the use of a
20 solvent-free polymer formulation, or a curable formulation. In certain simplified methods, a dry or liquid polymer formulation can be applied onto the proppant substrate via inline mixing, and the modified material thus prepared can be used without further processing. The moisture content of the proppant substrate can be modified by addition or removal of water, or addition of other liquids, to allow the substrate to be effectively
25 coated, handled, and delivered into the fracturing fluid.

[0045] The modified proppants can be further modified with a wetting agent such as a surfactant or other hydrophilic material to allow for effective dispersion into a fracturing fluid. When the hydrogel-modified proppants are suspended into a fracturing fluid, they are considered to be self-suspending if they require a lower viscosity fluid to prevent the
30 particles from settling out of suspension.

[0046] The modified proppants can be further modified with an anticaking agent such as calcium silicate, calcium carbonate, talc, kaolin, bentonite, diatomaceous earth, silica, colloidal silica, or microcrystalline cellulose to improve the flowability and handling properties of the modified proppant material. The modified proppants with the anticaking

agent can have improved handling properties, such as free-flowing properties, resistance to clumping, ease of conveying, ease of metering, and ease of discharging from a storage or transport vessel. In embodiments, the modified proppants with the anticaking agents can have reduced drying requirements, so that the finished product can be produced with a reduced amount of energy, time, and equipment.

5 [0047] The hydrogel-modified proppants of the invention can advantageously use a localized polymer concentration on the proppant surface, in contrast to the traditional approach of making the entire fluid medium viscous. This localized hydrogel layer can permit a more efficient use of polymer, such that a lower total amount of polymer can be used to suspend proppant, as compared, for example, with conventional polymer-enhanced fracturing fluids such as slickwater, linear gel, and crosslinked gel. Although 10 the hydrogel-modified proppants are considered to be self-suspending, they can be used in combination with friction reducers, linear gels, and crosslinked gels.

[0048] The hydrogel-modified proppants as disclosed herein can have the advantage of 15 delivering friction-reducing polymer into the fracturing fluid, so that other friction reducer polymers might not be required or might be required in lesser amounts when the hydrogel-modified proppants are used in hydraulic fracturing operations. In embodiments, some of the hydrogel polymer can desorb from the surface of the proppant to deliver friction reducing benefits or viscosity features to the fracturing fluid. While the 20 exemplary embodiments herein focus on the use of hydrogel-modified proppants for hydraulic fracturing purposes, other uses for hydrogel-modified proppants can be envisioned, where their capabilities for water retention or friction reduction can be exploited. For example, hydrogel-modified proppants can be used for absorbing water from moist environments, forming water-retaining particles that can be removed from the 25 environment, carrying with them undesirable moisture. As another example, hydrogel-modified proppants can be used in situations where adding water to an environment would be advantageous. A hydrogel-modified proppant can be saturated with water or an aqueous solution and then used, for example, as a soil remediation additive in a dry environment. The hydrogel-modified proppant can be formed from sand or other 30 substrates that are compatible with the soil, and they can be transported to the area of interest in dry form; they then can be saturated with water and used as a soil amendment. In other embodiments, hydrogel-modified proppants can be used as a soil amendment in dry form, where they can absorb and hold moisture from the environment, from irrigation, from rainfall and the like. In these embodiments, the moisture-holding properties of the

hydrogel-modified proppant can be used advantageously. In embodiments, the hydrogel-modified proppant can be used to reduce erosion of topsoil, seedbeds, hydroseeding mixtures, and the like. In embodiments, the hydrogel-modified proppant can be used as a vehicle for introducing other compatible agents into the region, for example into the soil.

5 Hydrogel-modified proppants can comprise additional formulations that leach out of or through the hydrogel layer into the environment, either as the hydrogel degrades, or as it absorbs moisture and expands. Examples of these formulations include fertilizers, seeds, plant growth regulators, herbicides, pesticides, fungicides, and the like. Other uses for hydrogel-modified proppants prepared in accordance with these formulations and
10 methods can be envisioned that are consistent with their properties described herein.

[0049] The hydrogel polymer used for preparation of hydrogel-modified proppants can, in embodiments, comprise polymers such as a polyacrylamide, copolymers of acrylamide with anionic and cationic comonomers, copolymers of acrylamide with hydrophobic comonomers, poly(acrylic acid), poly(acrylic acid) salts, carboxymethyl cellulose,
15 hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, alginate, carrageenan, locus bean gum, carboxymethyl guar, carboxymethyl hydroxypropyl guar gum, hydrophobically associating swellable emulsion (HASE) polymers, latex polymers, starches, and the like. In embodiments, the hydrogel polymer can be crosslinked to enhance the water absorbing and swelling properties of the polymer. The crosslinkers can
20 be introduced as an element of the hydrogel base polymer, or they can be introduced as chemical modifiers for pre-formed polymers.

[0050] Localizing the polymer around the proppant surface as described herein can result in a more effective use of polymer and can prevent proppant from settling out of a polymer solution. In embodiments, the polymer layer hydrates around the proppant
25 effectively preventing proppant/proppant (interparticle) contact. This can prevent the proppant from forming a compact settled bed and can result in a proppant that is easier to resuspend in a fracturing fluid. The resuspension properties for the modified proppants can be important if the fluid flow is interrupted during hydraulic fracturing operations. In this event, when the flow is resumed, it is important that the proppant can be resuspended
30 to avoid the loss of proppant or the unintended blockage of a fluid path.

[0051] The polymer surface modifications as described herein can cause an increase in the hydrodynamic radius of the proppant particle when the polymer swells. This can result in increased drag on the proppant as well as effectively changing the overall

hydrogel/particle density. Both can result in a proppant particle with a slower settling rate and superior transport properties.

[0052] In embodiments, polymer pairing or ionic crosslinking can be used to improve the hydrogel polymer retention on the surface of the proppant particles. For example, a cationic polymer can be deposited onto the proppant as a first layer to “lock in place” a second layer containing a hydrogel such as a high molecular weight anionic polymer. In 5
embodiments, the cationic polymer can be polydiallyldimethylammonium chloride (poly-(DADMAC)), linear polyethylenimine (LPEI), branched polyethylenimine (BPEI), chitosan, epichlorohydrin/dimethylamine polymer, ethylene dichloride dimethylamine 10
polymer, or cationic polyacrylamide. The cationic polymer layer can be placed on the proppant either before or after proppant surface modification with the anionic hydrogel layer. The ionic interaction can act as a crosslink mechanism to help prevent the anionic polymer from desorbing in high shear environments such as going through a pump or during pumping down the wellbore. The cationic polymer can also improve polymer 15
retention by causing a delay in the hydration and extension of the anionic polymer chains. It is believed that less polymer chain extension during the pumping process will yield higher polymer retention on the proppant (i.e. less desorption).

[0053] Covalent crosslinking of the hydrogel polymer layer on proppant surface can improve the swelling properties of the polymer and the shear tolerance to prevent 20
premature release of the hydrogel from the proppant. Covalent crosslinkers can include the following functional groups: epoxides, anhydrides, aldehydes, diisocyanates, carbodiamides, divinyl, or diallyl groups. Examples of these covalent crosslinkers include: PEG diglycidyl ether, epichlorohydrin, maleic anhydride, formaldehyde, glyoxal, glutaraldehyde, toluene diisocyanate, methylene diphenyl diisocyanate, 1-ethyl-3-(3- 25
dimethylaminopropyl) carbodiamide, methylene bis acrylamide. Covalent crosslinking of the hydrogel polymer layer on the proppant surface can effectively create a swellable “polymer cage” around the proppant. The covalent bonds prevent the polymer from completely desorbing into solution. The slightly insoluble polymer layer is able to swell and produce a hydrated polymer layer.

[0054] To further prevent the possible detachment of the hydrogel from the surface of 30
the particle, the proppant particle can be treated to impart functionalities that will also take part in the polymerization process. For example, sand particles can be treated with silanes to yield particles with vinyl functionalities, hydroxyl, epoxy, etc.

[0055] Delayed/controlled hydration of polymer layer may be desirable to delay the hydration of the polymer surface modification during handling of the proppant and initial pump-down through the wellbore. Environmental factors, such as humidity and rain, could cause premature hydration of the polymeric coating, which would make it difficult to effectively meter the proppant dose into the blender during a hydraulic fracturing operation. It is also believed that a fully hydrated polymer layer can be more prone to desorption under the high shear conditions associated with pumping of a fracturing fluid down the tubular. For these reasons, it may be advantageous to engineer a surface-modified proppant having slower or delayed hydration properties. In embodiments, delayed hydration can be achieved by addition of a low hydrophilic-lipophilic balance (HLB) surfactant, exclusion of a high HLB finishing surfactant, ionic crosslinking, covalent crosslinking, charge shielding using a monovalent salt, or by incorporation of a hydrophobic layer such as a fatty acid, or a fatty alcohol.

[0056] In embodiments, hydrophobic groups can be incorporated into the hydrogel polymer to allow for hydrophobic interactions. This method can improve the salt tolerance of the hydrogel layer, such that the hydrogel layer remains swellable even in an aqueous fluid that contains elevated salt concentrations.

[0057] Also disclosed herein is a method of improving well productivity by improved proppant placement using a hydrogel-coated proppant. The hydrogel-coated proppant can be more effectively transported into the far end of fractures to enable higher productivity of oil and gas from a well. Because the surface-modified proppants disclosed herein can be less inclined to settle out of the fluid and easier to resuspend and transport through the fracture, it is believed that proppant placement will be more effective. The ability to transport proppant further into fractures could significantly increase the effectiveness of a fracturing stimulation operation, resulting in a larger of volume of higher density fractures. These fracture channels can advantageously allow gas/condensate to more easily flow into the wellbore from the reservoir.

[0058] Also disclosed herein is an improved method of proppant placement using a low viscosity fluid. The surface modified proppants as disclosed herein utilize polymers more effectively to suspend/transport proppant particles. The surface modification renders the proppant self-suspending, thereby reducing or eliminating the need for highly viscous fluids/gels to transport proppant. Hence, lower viscosity fluids can be used in combination with the surface-modified proppant to transport proppant into fractures. This would advantageously simplify the formulation of fracturing gels for use with proppants.

[0059] Also disclosed herein is a more efficient method of fracturing a well using less proppant. Because highly effective proppant placement can be achieved with the easily-transportable surface-modified proppants as disclosed herein, it is anticipated that a smaller amount of these surface-modified proppants would be required for any given
5 fracturing operation, as compared to systems using traditional proppants. With an increasing demand for fracturing grade sand/proppants, and a decreasing supply of desirably-shaped sand for proppant use, it would be advantageous to provide systems and methods such as those disclosed herein where less proppant can be used to achieve results comparable to or superior to the outcomes using current techniques.

10 [0060] After the hydrogel coated proppants of the invention have been pumped into a well, the hydrogel layer can be degraded by chemical, thermal, mechanical, and biological mechanisms. Specifically, the polymeric surface modification on the proppant can be broken down with the aid of chemical breakers, for example, ammonium persulfate or other oxidizers. Controlled breaking of the hydrogel layer upon reaching a
15 target temperature or amount of time in the fluid, can be used as a means to direct the placement of the proppant in the desired location in fractures. The degradation of the hydrogel layer is also beneficial to ensuring the adequate conductivity of the propped fracture after completing the hydraulic fracturing operations.

[0061] Also disclosed herein is a method of delivery of additives, for example, chemical
20 additives, into the proppant pack, by incorporating the additives into the hydrogel layer of the modified proppant. The additives can include chemical additives that can be advantageously delivered in the hydrogel layer, for example scale inhibitor, biocide, breaker, wax control, asphaltene control, and tracers. In embodiments, these chemical additives can be chemically bound to the polymer in the hydrogel layer, for example by
25 covalent bonding, ionic bonding, hydrophobic association, hydrogen bonding, and the like. After placement in a proppant pack, the desorption, oxidation, or degradation of the hydrogel polymer can result in the controlled release of the chemical additives from the self-suspending proppant. In embodiments, a hydraulic fracturing operation can have multiple stages of fracturing; the proppants injected in each stage can contain unique
30 tracers. Analysis of the fluids produced from the fractured well can provide information about the relative productivity of each fracturing stage by the presence and concentration of the unique tracers corresponding to the stages. In other embodiments, additives, for example, particulate additives, can be physically bound or entangled in the polymer layer.

[0062] In embodiments, the surface of a proppant particulate substrate can be coated with a selected polymer, either as a single layer or as a series of multiple coating layers. The coating (either single layer or multilayer) can show switchable behavior under certain circumstances. As used herein, the term “switchable behavior” or “switching behavior”
5 refers to a change in properties with a change in circumstances, for example, a change from one set of properties during the transport phase and another set of properties inside the fracture. Switching behavior can be seen, for example, when a particle demonstrates hydrophilic properties in the fracturing fluid and adhesive properties when in place within the fractures. Such behavior can be triggered by circumstances like the high closing
10 pressures inside the fracture site so that the outer layer of the coating rearranges itself to exhibit more advantageous properties.

[0063] In an embodiment, the coated particle can switch from hydrophilic to hydrophobic when subjected to the high pressures inside the fractures. In an exemplary embodiment, during the transport phase, when the hydrophilic covering of the particle is
15 exposed to the water-based fracturing fluid, it will tend to be fully distended. As a result, the coating can provide the particle with lubrication in this state, facilitating its movement through the proppant slurry. When the particle has been conveyed to its destination within the fractures in the formation though, the high pressures there will overcome the steric repulsions of the external hydrophilic polymer chains, forcing the outer layer to
20 rearrange itself so that the inner layer is exposed. In embodiments, the switchable inner layer can be hydrophobic or adhesive, or both. As the inner layer becomes exposed, its properties can manifest themselves. If the inner layer has adhesive properties, for example, it can fix the particles to each other to prevent their flowback. This inner layer can also be configured to capture fines in case the proppant particle fails. Moreover, the
25 residual intact hydrophilic groups present in the outer coating can allow easy flow of oil through the proppant pack.

[0064] In embodiments, a coated proppant particle can be produced that bears the following layers of coating. First, a pressure-activated fixative polymer can be used to coat the proppant substrate. This coating layer can be elastomeric, thereby providing
30 strength to the proppant pack by helping to agglomerate the proppant particles and distribute stress. In addition, this coating layer can encapsulate the substrate particles and retain any fines produced in the event of substrate failure. Second, a block copolymer can be adsorbed or otherwise disposed upon the first layer of coating. The copolymer can have a section with high affinity for the first polymeric layer, allowing strong interaction

(hydrophobic interaction), and can have another section that is hydrophilic, allowing for easy transport of the proppant in the transport fluid.

5 [0065] In certain embodiments, a stronger interaction between the first and second coating layers may be useful. To accomplish this, a swelling-deswelling technique can be implemented. For example, the block copolymer can be adsorbed onto the surface of the elastomeric-coated particle. Then, the first coating layer can be swelled with small amounts of an organic solvent that allow the hydrophobic block of the copolymer to penetrate deeper into the first coating layer and to become entangled in the elastomeric coating. By removing the organic solvent, the layered polymeric composite will deswell, resulting in a stronger interaction of copolymer with the elastomeric particle. A method for swelling-deswelling technique that can be useful is set forth in "Swelling-Based Method for Preparing Stable, Functionalized Polymer Colloids," A. Kim et al., J. Am. Chem. Soc. (2005) 127: 1592-1593, the contents of which are incorporated by reference herein.

15 [0066] While the systems described herein refer to a two-layer coating system, it is understood that there can be multiple (i.e., more than two) coating layers forming the composite proppant particles disclosed herein, with the each of the multiple coating layers possessing some or all of the attributes of the two coating layers described above, or with one or more of the multiple coating layers providing additional properties or features.

20 [0067] The addition of a species capable of crosslinking the swellable polymer on the proppant surface can effectively reduce the ability of the polymer layer to swell prematurely. Decreased swelling of the polymer can reduce the tendency of the polymer-coated proppant to undergo caking during storage in humid conditions. As used herein, the term "caking" refers to the formation of clumps or solid masses by adhesion of the loose granular material. Caking of proppants during storage is undesirable for material handling purposes. Preferably, the crosslinker will not impede hydration/swelling of the polymer coating once the polymer-coated proppant is dispersed in an aqueous fluid, such as a hydraulic fracturing fluid. In embodiments, the crosslinking species has the capability of forming a bond with a carboxyl functional group, an amide functional group, or both. Preferably, the crosslinking species forms a bond that can be broken or removed under mechanical shear or by the action of a chemical breaker. The crosslinking species can be added directly into the polymer used to coat the proppant, simultaneously added to the proppant with the polymer while mixing, or added some time after addition of the polymer to the proppant but before drying.

[0068] The crosslinking species can be chosen from organic compounds containing aldehyde, amine, anhydride, or epoxy functional groups. The crosslinking species can also be an organometallic compound. Organometallic compounds able to associate and/or bond with the carboxyl functional group are an example of a crosslinking species that
5 form shear sensitive bonds. In such embodiments, the organometallic compound is able to reduce the swelling tendency of the polymer-coated proppant via crosslinking the carboxyl groups prior to the introduction of the proppant into a hydraulic fracturing fluid. Then, when the crosslinked polymer coating encounters the high shear forces of pumping associated with hydraulic fracturing, the crosslink on the polymer can be degraded,
10 allowing the polymer is able to swell unhindered when the proppant is introduced into the hydraulic fracturing fluid.

[0069] In certain embodiments, a thin, non-hygroscopic coating layer can be applied to the surface of a hydrogel-coated proppant to create a barrier preventing the swellable polymer layer on adjacent proppant particles from adhering during storage. The outer
15 layer utilized can be comprised of compounds that are water-soluble, water insoluble or both. In embodiments, the outer layer can be formulated such that it remains in the solid phase at temperatures below 40°C and has a melting point in the range of 40°C to 120°C. Preferably the outer layer is formulated such that the melting point is low enough that the outer layer will be in the liquid phase during the drying process in the manufacturing of
20 the polymer coated proppant, yet is high enough that the outer layer will exist in the solid phase during storage and transport of the polymer coated proppant.

[0070] In these embodiments, the outer layer acts as a barrier to reduce caking of the coated proppant in humid environments. The hydrophobic outer layer can be added to the polymer-coated proppant as a finely divided powder or as a liquid. In embodiments, the
25 outer layer material can be melted prior to addition to the coated proppant; in other embodiments the outer layer material can be added as a solid or waxy material, which can melt during the drying process. The solid outer layer can be added to the proppant simultaneously with the polymer or can be added at some time after addition of polymer but before the drying process. The outer layer can be comprised of fatty acids,
30 hydrogenated oils, vegetable oils, castor oil, waxes, polyethylene oxides, polypropylene oxides, and the like.

2. Particulate Substrate Materials

[0071] Composite proppant particles in accordance with these systems and methods can be formed using a wide variety of proppant substrate particles. Proppant particulate substrates can include for use in the present invention include graded sand, resin coated sand, bauxite, ceramic materials, glass materials, walnut hulls, polymeric materials, 5 resinous materials, rubber materials, and the like. In embodiments, the substrates can include naturally occurring materials, for example nutshells that have been chipped, ground, pulverized or crushed to a suitable size (e.g., walnut, pecan, coconut, almond, ivory nut, brazil nut, and the like), or for example seed shells or fruit pits that have been 10 chipped, ground, pulverized or crushed to a suitable size (e.g., plum, olive, peach, cherry, apricot, etc.), or for example chipped, ground, pulverized or crushed materials from other plants such as corn cobs. In embodiments, the substrates can be derived from wood or processed wood, including but not limited to woods such as oak, hickory, walnut, mahogany, poplar, and the like. In embodiments, aggregates can be formed, using an 15 inorganic material joined or bonded to an organic material. Desirably, the proppant particulate substrates will be comprised of particles (whether individual substances or aggregates of two or more substances) having a size in the order of mesh size 4 to 100 (US Standard Sieve numbers). As used herein, the term "particulate" includes all known shapes of materials without limitation, such as spherical materials, elongate materials, 20 polygonal materials, fibrous materials, irregular materials, and any mixture thereof.

[0072] In embodiments, the particulate substrate can be formed as a composite from a binder and a filler material. Suitable filler materials can include inorganic materials such as solid glass, glass microspheres, fly ash, silica, alumina, fumed carbon, carbon black, graphite, mica, boron, zirconia, talc, kaolin, titanium dioxide, calcium silicate, and the 25 like. In certain embodiments, the proppant particulate substrate can be reinforced to increase their resistance to the high pressure of the formation which could otherwise crush or deform them. Reinforcing materials can be selected from those materials that are able to add structural strength to the proppant particulate substrate, for example high strength particles such as ceramic, metal, glass, sand, and the like, or any other materials 30 capable of being combined with a particulate substrate to provide it with additional strength.

[0073] In addition to bare or uncoated substrates, composite hydrogel-coated proppants can be formed from substrates that have undergone previous treatments or coatings. For example, a variety of resin-coated proppant particles are familiar to skilled artisans. The

formulations and methods described above for coating are suitable for use with coated or treated proppant particles, including curable and precured resin coated proppants.

[0074] In one embodiment for treating resin-coated sand, a swellable hydrogel layer, as described above, can be applied to the resin-coated sand to improve its suspension

5 characteristics. In embodiments, one can include the addition of the species that acts as an adhesion promoter to attach the hydrogel to the resin layer. The adhesion promoters can be, for example, block co-polymers composed of both hydrophilic and hydrophobic monomers. The block co-polymer can be added after the substrate sand is resin-coated or at the same time as the resin coating. In addition to block co-polymers, cationic species

10 can be used such as fatty amines, polyquaternary amines, and cationic surfactants.

[0075] In certain embodiments, the proppant particulate substrate can be fabricated as an aggregate of two or more different materials providing different properties. For example, a core particulate substrate having high compression strength can be combined with a buoyant material having a lower density than the high-compression-strength material.

15 The combination of these two materials as an aggregate can provide a core particle having an appropriate amount of strength, while having a relatively lower density. As a lower density particle, it can be suspended adequately in a less viscous fracturing fluid, allowing the fracturing fluid to be pumped more easily, and allowing more dispersion of the proppants within the formation as they are propelled by the less viscous fluid into more

20 distal regions. High density materials used as proppant particulate substrates, such as sand, ceramics, bauxite, and the like, can be combined with lower density materials such as hollow glass particles, other hollow core particles, certain polymeric materials, and naturally-occurring materials (nut shells, seed shells, fruit pits, woods, or other naturally occurring materials that have been chipped, ground, pulverized or crushed), yielding a

25 less dense aggregate that still possesses adequate compression strength.

[0076] Aggregates suitable for use as proppant particulate substrates can be formed using techniques to attach the two components to each other. As one preparation method, a proppant particulate substrate can be mixed with the buoyant material having a particle size similar to the size of the proppant particulate substrates. The two types of particles

30 can then be mixed together and bound by an adhesive, such as a wax, a phenol-formaldehyde novolac resin, etc., so that a population of doublet aggregate particles are formed, one subpopulation having a proppant particulate substrate attached to another similar particle, one subpopulation having a proppant particulate substrate attached to a buoyant particle, and one subpopulation having a buoyant particle attached to another

buoyant particle. The three subpopulations could be separated by their difference in density: the first subpopulation would sink in water, the second subpopulation would remain suspended in the liquid, and the third subpopulation would float.

[0077] In other embodiments, a proppant particulate substrate can be engineered so that it is less dense by covering the surface of the particulate substrate with a foamy material. The thickness of the foamy material can be designed to yield a composite that is effectively neutrally buoyant. To produce such a coated proppant particulate, a particle having a desirable compression strength can be coated with one reactant for a foaming reaction, followed by exposure to the other reactant. With the triggering of foam formation, a foam-coated proppant particulate will be produced.

[0078] As an example, a water-blown polyurethane foam can be used to provide a coating around the particles that would lower the overall particle density. To make such a coated particle, the particle can be initially coated with Reactant A, for example a mixture of one or more polyols with a suitable catalyst (e.g., an amine). This particle can then be exposed to Reactant B containing a diisocyanate. The final foam will form on the particle, for example, when it is treated with steam while being shaken; the agitation will prevent the particles from agglomerating as the foam forms on their surfaces.

[0079] The crosslinking species can be added directly into the polymer used to coat the proppant, simultaneously added to the proppant with the polymer while mixing, or added some time after addition of the polymer to the proppant but before drying.

EXAMPLES

Materials

- 30/70 mesh frac sand
- 40/70 mesh frac sand
- Polydiallyldimethylammonium chloride (Aldrich, St. Louis, MO)
- LPEI 500 (Polymer Chemistry Innovations, Tucson, AZ)
- Ethyl Alcohol, 200 Proof (Aldrich, St. Louis, MO)
- Hexane (VWR, Radnor, PA)
- FLOPAM EM533 (SNF)
- Polyethyleneglycol diglycidyl ether (Aldrich, St. Louis, MO)
- Glyoxal, 40wt% solution (Aldrich, St. Louis, MO)
- HFC-44 (Polymer Ventures)
- Carboxymethyl Cellulose, sodium salt (Sigma-Aldrich, St Louis, MO)

- Ammonium Persulfate (Sigma-Aldrich, St. Louis, MO)
- Ethoxylated lauryl alcohol surfactant (Ethal LA-12/80%) (Ethox Chemical Co, SC)
- Phenolic resin coated frac sand from a commercial source
- SMA 4000i, from Sartomer
- 5 • SMA 2000i, from Sartomer
- Pluronic Surfactant L31, from BASF, Florham Park, NJ
- Pluronic Surfactant L35, from BASF, Florham Park, NJ
- Pluronic Surfactant L81, from BASF, Florham Park, NJ
- ARQUAD® 2HT-75, from Sigma Aldrich, St. Louis, MO
- 10 • ADOGEN® 464, from Sigma Aldrich, St. Louis, MO
- Isopropanol (IPA), manufactured by Sigma Aldrich, St. Louis, MO
- Tetrahydrofuran (THF), manufactured by Sigma Aldrich, St. Louis, MO
- Glycerol, manufactured by Sigma Aldrich, St. Louis, MO
- 30/50 mesh white sand
- 15 • Thixcin-R (Elementis Specialties)
- Castor oil (J.T. Baker)
- Stearic Acid Powder (J.T. Baker)
- Tyzor TE (Dorf Ketal)
- Tyzor TEAZ (Dorf Ketal)

20 **[0080]** Example 1: Preparation of Inner Polymer Layer

[0081] An inner polymer layer of 100 ppm concentration was prepared on a sand sample by adding 200g 30/70 mesh frac sand to a FlackTek Max 100 long jar. To the sand was added 85 g tap water and 2 g of a 1% polydiallyldimethylammonium chloride (PDAC) solution. The sample was then shaken by hand for approximately 5 minutes, vacuum
25 filtered and dried in an oven at 80°C. The sand sample was then removed from the oven and used in subsequent testing.

[0082] An identical method was used as described above to formulate a 10ppm inner polymer layer coating with the exception being that only 0.2 g of a 1% PDAC solution were used.

30 **[0083]** An identical method was used as described above to formulate an inner polymer layer at a maximum polymer loading (“Max PDAC”) with the exception that 1 g of a 20wt% PDAC solution was used. Following treatment the sand was washed with excess

tap water, vacuum filtered and dried in an oven at 80°C. The sand sample was then removed from the oven and used in subsequent testing.

[0084] Example 2: Preparation of Inner Polymer Layer

[0085] An inner polymer layer of 100 ppm concentration was prepared on a sand sample by dissolving 0.2 g LPEI 500 in 10 g ethanol to form a 2% LPEI 500 solution in ethanol. To 70 g ethanol in a 250 mL round bottom flask was added 0.75 g of the 2% LPEI 500 solution. Then 150 g of 30/70 mesh frac sand was added to the round bottom flask. The solvent was removed using a rotary evaporator with a 65°C water bath. The sample was then removed from the flask and used in subsequent testing.

10 [0086] Example 3: Preparation of Outer Polymer Layer

[0087] Outer polymer layers were applied to sand samples by mixing sand with liquid Flopam EM 533 polymer under different conditions. In one coating method, polymer product was added neat. In another coating method the polymer product was extended by diluting with hexane. For hexane dilution 10 g polymer was added to 10 g hexane in a 40 mL glass vial and vortex mixed until homogenous. Polymer was then added to 30/70 mesh frac sand samples of 30 g in FlackTek Max 100 jars. Samples were placed in a FlackTek DAC150 SpeedMixer at 2600 rpm for about 25 seconds. Samples were removed from SpeedMixer and allowed to dry in an oven at 80°C overnight.

[0088] Example 4: Performance of Outer Polymer Layer, Settling Times

20 [0089] Sand samples prepared in previous example were assessed for performance in a settling test. Prior to testing, all sand samples were sieved through a 25 mesh screen. Settling times were obtained by adding 1 g of sand sample to 100 mL of tap water in a 100 mL graduated cylinder. The graduated cylinder was then inverted about 8 times and then the time required for all of the sand to settle at the bottom of the graduated cylinder was recorded. Three times were recorded for each sample. Settling times are reported in Table 1.

Table 1 Settling Times

Sample	Inner Layer	Outer Layer Treatment	Treatment Added (g)	Settling Time1 (sec)	Settling Time2 (sec)	Settling Time3 (sec)
1	100ppm PDAC	Flopam EM533	1	34	35	32
2	100ppm PDAC	50:50 Flopam EM533/hexane	2	25	25	26

Sample	Inner Layer	Outer Layer Treatment	Treatment Added (g)	Settling Time1 (sec)	Settling Time2 (sec)	Settling Time3 (sec)
3	100ppm PDAC	Flopam EM533	3	35	71	60
4	100ppm PDAC	50:50 Flopam EM533/hexane	6	24	33	32
5	Max PDAC	Flopam EM533	1	19	21	27
6	Max PDAC	50:50 Flopam EM533/hexane	2	17	23	21
7	Max PDAC	Flopam EM533	3	29	31	35
8	Max PDAC	50:50 Flopam EM533/hexane	6	23	24	25
9	None	Flopam EM533	1	22	22	22
10	None	Flopam EM533	3	25	54	64
11	None	None	0	10	10	10

[0090] Example 5: Performance of Outer Polymer Layer, Settled Bed Height

[0091] Sand samples prepared in Example 3 with outer polymer layer were also assessed by observing the settled bed height in water. In a 20 mL glass vial, 1 g of a sand sample was added to 10 g tap water. The vials were inverted about 10 times to adequately wet the sand treatments. The vials were then allowed to sit undisturbed for about 30 minutes. A digital caliper was then used to record the height of the sand bed in the vial. Results are reported in Table 2.

10 **Table 2 Settled Bed Heights**

Sample	1	2	3	4	5	6	7	8	9	10	11
Bed Height (mm)	13.5	6.9	22.6	8.9	8.9	5.8	11.9	n/a	11.9	22.9	0.8

[0092] Example 6: Ionic Crosslink of Outer Polymer Layer

[0093] A 40g 30/70 mesh frac sand sample was treated with an outer polymer layer by adding 1.3 g Flopam EM 533 polymer to the 40 g of sand in a FlackTek Max 100 jar and shaking the jar by hand for 2 minutes. The sand was then sieved through a 25 mesh
 5 screen. To assess polymer retention on sand under shear, tests were conducted by adding 10 g of treated sand to 200 g tap water with different levels of PDAC in a 300 mL glass beaker. It is believed that the PDAC will interact ionically to stabilize the polymer layer on the sand. The slurries were then stirred at 900 rpm with an overhead mixer using a flat propeller style mixing blade for 5 minutes. Mixing was then stopped and samples were
 10 allowed to settle for 10 minutes. Viscosity of the supernatant was then measured using a Brookfield DV-III+ rheometer with an LV-II spindle at 60 rpm. Bed height of the settled sand in the beaker was also recorded using a digital caliper. Results are reported in Table 3.

15

Table 3 Polymer Retention

Sample	PDAC Conc. (ppm)	Visc. (cP)	Bed Height (mm)
12	0	25	4.5
13	60	10	8.6
14	200	2.5	6.3

[0094] Example 7: Covalent Crosslink of Outer Polymer Layer – PEGDGE

[0095] Four samples of 30/70 mesh frac sand were treated with Flopam EM 533 by adding 0.66 g polymer to 20 g sand in a FlackTek Max 100 jar and shaking by hand for 2
 20 minutes. Then various amounts of a fresh 1% polyethyleneglycol diglycidyl ether solution in deionized water were added to the treated sand samples. The samples were again shaken by hand for 2 minutes and then placed in an oven at 100°C for 1 hour. Samples were then removed from the oven and sieved through a 25 mesh screen. Bed heights were measured for the four samples by adding 1 g of the sand sample to 10 g of
 25 tap water in a 20 mL glass vial, inverting the vials approximately 10 times to adequately wet the sand and allowing the vials to sit undisturbed for about 10 minutes. Bed heights were then measured with a digital caliper. Results are listed in Table 4.

Table 4 PEGDGE Treated Outer Polymer Layer

Sample	1% PEGDGE (g)	Bed Height (mm)
15	0.1	9.3
16	0.2	8.8
17	1.0	6.2
18	0	12.7

[0096] Example 8: Covalent Crosslink of Outer Polymer Layer – Glyoxal

[0097] Four samples of 30/70 mesh frac sand were treated with Flopam EM 533 by adding 0.66 g polymer to 20 g sand in a FlackTek Max 100 jar and shaking by hand for 2 minutes. A 1% glyoxal solution in ethanol was formulated by adding 0.25 g 40 wt% glyoxal to a 20 mL glass vial and diluting to 10 g with ethanol. Then varying amounts of the 1% glyoxal solution were added to the treated sand samples, and the samples were shaken by hand for 2 minutes and placed in the oven at 100°C for 30 minutes. The sand samples were removed from the oven and sieved through a 25 mesh screen. For settled bed height measurements 1 g of sand was added to 10 g tap water in 20 mL vials, inverted about 10 times and given about 10 minutes to settle. Bed height was measured with a digital caliper. Results are listed in Table 5.

Table 5 Glyoxal Treated Outer Polymer Layer

Sample	1% glyoxal (g)	Bed Height (mm)
19	0.2	3.8
20	0.5	3.5
21	1.0	2.7
22	2.0	2.7

[0098] Example 9: Cationic/Anionic polymer treatments

[0099] Three samples of 30 g of 30/70 mesh frac sand were treated with Polymer Ventures HCF-44 in a FlackTek Max 100 jar. The jar was shaken by hand for 2 minutes. Flopam EM 533 was then added to each of the samples. The jars were again shaken by hand for 2 minutes. The samples were then dried at 80°C overnight. The sand samples were removed from the oven and sieved through a 25 mesh screen. For settled bed height measurements 1 g of sand was added to 10 g tap water in 20 mL vials, inverted about 10

times and given about 10 minutes to settle. Bed height was measured with a digital caliper. Results are given in Table 6.

Table 6 Cationic/Anionic polymer treatment

Sample	HCF-44 (g)	Flopam EM 533 (g)	Bed Height (mm)
23	0	0.45	10.26
24	0.07	0.38	8.08
25	1.0	0.35	5.08
26	1.5	0.30	3.94

5

[00100] Example 10: Sand coated with macromolecular particles

[00101] A 30 g sample of 30/70 mesh frac sand was added to a FlackTek Max 100 jar. To the sand, 0.3g of paraffin wax was added. The sample was placed in a FlackTek DAC 150 SpeedMixer and mixed at 2500 rpm for 2 minutes. After mixing, 1 g of carboxymethyl cellulose was added to the sample. The sample was again placed in the FlackTek DAC 150 SpeedMixer and mixed at 2500 rpm for 1 minute. The sand sample was sieved through a 25 mesh screen. For settled bed height measurements 1 g of sand was added to 10 g tap water in a 20 mL vial, inverted about 10 times and given about 10 minutes to settle. The sand in this sample clumped together immediately and did not disperse in the water, and an accurate measurement of bed height could not be obtained.

15

[00102] Example 11: Modified sand beaker testing

[00103] A 30 g sample of 30/70 mesh frac sand was added to a FlackTek Max 100 jar. The sand was treated with Flopam EM 533 by adding 0.45g of the polymer to the jar and shaking by hand for 2 minutes. The sample was then dried at 80°C overnight. After drying, the sample was removed from the oven and sieved over a 25 mesh screen. After sieving, four samples were prepared by adding 1 g of the treated sand to 10 g of tap water in a 20 mL vial. The vials were inverted about 10 times and left to settle for 10 minutes. A 10% ammonium persulfate solution was made by adding 2 g of ammonium persulfate to 18 g of tap water. Varying amounts of the 10% ammonium persulfate solution were then added to the sample vials. The samples were inverted several times to mix, and then placed in an oven at 80°C for 1 hr. After 1 hour the samples were removed and the settled bed heights were observed. Table 7 shows the results.

20

25

Table 7 Breaker testing

Sample	10% APS (μm)	Sand Suspension
27	0	Suspended
28	180	Settled
29	90	Settled
30	18	Settled

[00104] Example 12: Emulsion Additives

[00105] To determine the effect of emulsion additives on self-suspending proppant (“SSP”) performance, we added glycerol and Ethal LA-12/80% to the emulsion polymer EM533 before coating the proppant sand. Three different polymer samples were made as follows:

- SSP Polymer: 10g of EM533, no additive
- SSP + glycerol: 9g EM533 and 1g of glycerol
- 10 • SSP + glycerol + Ethal: 9g EM533 + 0.9g glycerol + 0.1g Ethal LA-12/80%.

[00106] Each of the above samples was vortex mixed for 30s to ensure homogeneity. To make the modified proppant, 50g of 40/70 sand was combined with 1.5g of one of the polymer samples above and then mixed for 30s. The modified proppant samples were evaluated for shear stability in the 1 liter shear test. This test involves addition of 50 grams of modified proppant to 1 liter of water in a square plastic beaker, followed by mixing on a paddle/jar mixer (EC Engineering model CLM-4) at 200 rpm for different amounts of time. The sheared samples are then poured into a 1000 mL graduated cylinder and allowed to settle by gravity for 10 minutes, then the bed height of the settled proppant sand is recorded. For comparison, an unmodified proppant sand will produce a bed height of 10 mm after any amount of mixing. The self-suspending proppant samples will produce a higher bed level vs. unmodified proppant due to the hydrogel layer encapsulating the sand grains. Generally, increasing the shear rate or time can cause the bed height of self-suspending proppant to decrease as a result of desorption of the hydrogel layer from the surface of the modified proppant. For this reason, it is desirable for the bed height to be as high as possible in this test, especially after shear. The results below show that the addition of glycerol improves the bed height and the shear stability of the product. The addition of glycerol and Ethal, while it improves the initial bed height, the long term shear stability is slightly decreased. These results are illustrated in FIG. 2.

[00107] Example 13: Glycerol and Processability

[00108] This experiment sought to determine the effect of glycerol and other additives on the performance of self-suspending proppants (denoted as SSP below). 1 kg of dry 40/70 sand was added to the bowl of a KitchenAid stand mixer, model KSM90WH, which was fitted with the paddle attachment. 3.09 g of glycerol was mixed with 27.84 g of EM533 emulsion polymer, then the mixture was added to the top of the sand and allowed to soak in for 1 minute. At time 0 the mixer was started at speed 1 (72 rpm primary rotation). Samples were collected at 1-2 minute intervals and dried for 1 hour at 90°C. Then, each sample was subjected to the 1 liter shear test, where 50g of SSP was added to 1 L of water and sheared at 200 rpm (an approximate shear rate of 550 s⁻¹) for 20 minutes. After transferring the water/SSP mixture to a 1 liter graduated cylinder and settling for 10 min, the bed heights were recorded. The experiment was repeated with 30.93 g EM533 emulsion polymer alone added to 1 kg of sand. These results are shown in FIG. 3.

[00109] As shown in FIG. 3, the glycerol additive increased bed heights significantly.

[00110] The difference in performance was even more marked when the experiment was repeated at higher mixing speeds. Here the mixer was set to speed 4 (150 rpm primary rotation). At low mixing times, the samples were insufficiently mixed, leading to incomplete coating of the sand and ready desorption of the polymer from the surface of the SSP during the shear test. As mixing time of the coating process increased so did performance, until an ideal coating was reached, giving maximum bed height for that sample. After that, increasingly worse (lower) bed heights were seen at higher mixing times, possibly as a result of abrasion of the coating during extended mixing. At higher mixing speeds, this process happened even faster, such that the processing window for the emulsion polymer alone was less than 1 minute. With the addition of glycerol and the use of a lower mixing speed, this processing window was widened to nearly 15 minutes. In comparison to the tests with emulsion polymer alone, glycerol caused the processing window to widen, indicating that SSP preparation with the glycerol is more robust. At the same time, glycerol allowed the polymer emulsion to invert more fully, leading to better coatings and increased bed heights. Testing with combinations of glycerol and the emulsion polymer EM533 at a higher mixing speed yielded the results shown in FIG. 4.

[00111] Example 14: Modified proppant with an anticaking agent

[00112] Modified proppant samples were made with and without anticaking agent for a comparison. For Sample A, 50g of 40/70 sand was added to a FlackTek jar. 1.5g of

EM533 emulsion polymer was added to the sand and the sample was mixed for 30 seconds. After mixing, 0.25g of calcium silicate was added to the sample and the sample was mixed again for 30 seconds. The sample was then dried for 1 hour at 85°C. After drying, the sample was poured over a 25 mesh screen and shaken lightly for 30 seconds.

5 The amount of sand that passed through the sieve was then measured. For Sample B, 50g of 40/70 sand was added to a FlackTek jar. 1.5g of EM533 emulsion polymer was added to the sand and the sample was mixed for 30 seconds. The sample was then dried for 1 hour at 85°C. After drying, the sample was poured over a 25 mesh screen and shaken lightly for 30 seconds. The amount of sand that passed through the sieve was then

10 measured. Table 8 shows the results.

Table 8

Sample	Total Mass Sample, g	Mass passing Sieve, g	% Passing Sieve
Sample A	50.5	50.16	99.3%
Sample B	50.5	15.71	31.1%

[00113] The results of sieve testing show that the incorporation of an anticaking agent

15 was effective at improving the handling properties of the modified proppants.

[00114] Samples A and B were separately added to 1L of water and then sheared in the EC Engineering Mixer for 20 minutes at 200 rpm. After shearing, the samples were transferred to a 1 L graduated cylinder and left to settle for 10 minutes. After settling, the bed heights were measured, showing no significant loss in shear stability as a result of

20 incorporating an anticaking agent. Table 9 shows these results.

Table 9

Sample	Bed Height, mm
Sample A	56.21
Sample B	59.67

[00115] Example 15: Hydrogel coating of sand by dissolving a water-soluble polymer in a monomer formulation followed by polymerization of the monomers

25 [00116] 2.5 g of a mixture of acrylic acid (Aldrich 147230), poly(ethylene glycol) methyl ether acrylate (Aldrich 454990), and polyethylene glycol dimethacrylate (Aldrich 437441) in a mol ratio: 0.5/0.4/0.1 can be mixed with 7.5 g of polyethylene glycol

(Aldrich 202371) and 1 wt% of ammonium persulfate. The solution can be mixed with 100 g of 30/70 mesh sand under nitrogen and can be allowed to react by increasing the temperature to 70°C for 5 hours. Next the solids obtained are washed with methanol, vacuum filtered and dried in an oven at 80°C.

5 [00117] Example 16: Polyurethane hydrogel coating of sand

[00118] 100 g of 30/70 mesh frac sand can be added to a Hobart type mixer and heated to 120°C. Next 6 g of a polyethyleneglycol (Fluka 81190) will be added and allowed to mix for 1 minute. Then 0.53 g of Desmodur N75 from Bayer will be added. After mixing for 1 more minute, one drop of catalyst 1,4-Diazabicyclo[2.2.2]octane (Aldrich D27802) will
10 be added and the mixture will be allowed to react for 5 more minutes. The obtained solid is washed with methanol, vacuum filtered and dried in an oven at 80°C.

[00119] Example 17: Hydrogel coating of sand by admicellar polymerization

[00120] 250 g of 30/70 frac sand can be added to 500 ml of a previously degassed aqueous solution containing 0.6 mM hexadecyltrimethylammonium bromide (CTAB) surfactant (equivalent to 2/3 of the critical micelle concentration of CTAB), and 6 mM
15 monomer (mixture of acrylic acid/acrylamide in a mol ratio 30/70). Adsorption of the CTAB and monomer onto the sand particle can be carried out under gentle stirring for 24 h at 25°C. Then, 0.6 mM Ammonium persulfate can be added to the reactor and the polymerization will take place for 3 h at 80°C. Excess polymer and surfactant can be
20 rinsed with several volumes of water and the sample will be dried overnight in the vacuum oven at 80°C.

[00121] Example 18: Hydrogel coating of sand by inverse suspension polymerization

[00122] To a flask can be added 60 ml of DI-water, 6.6 g acrylamide, 3 g of acrylic acid, 2.4 g of N,N'-methylenebisacrylamide, 0.1 g ammonium persulfate, 2.0 g sodium
25 chloride and 2 drops of N, N, N', N'-tetramethylethylenediamine. To this solution can be added 200 g of 30/70 mesh frac sand and the whole mixture will be kept at temperature <10°C. To the mixture can be added 200 ml of cyclohexane and the whole mixture can be vigorously stirred under nitrogen. Next the temperature can be increased to 60°C and the reaction allowed to proceed for 6 hours. The resultant coated particles can be filtered
30 and washed with hot water, acetone and dried at 45°C under reduced pressure.

[00123] Example 19: Coating Polymer

[00124] A mixture for coating the proppant was made by mixing SNF Flopam EM 533 and glycerol in a 9:1 ratio. This polymer mixture is used in following examples.

[00125] Example 20: Preparation of 40/70 mesh self-suspending proppant (“SSP”)

[00126] A sample of 40/70 mesh size SSP was prepared by adding 500 g of 40/70 frac sand into the bowl of a KitchenAid mixer. 20 g of the coating polymer of Example 19 was added to the sand. The mixer was turned on at a setting of 1 and the sand and polymer mixture mixed for 7 minutes. After mixing, the sample was dried for 1 hour at 85°C. After 1 hour, the sample was removed from the oven and any lumps were broken into individual grains.

[00127] Example 21: Preparation of 30/50 mesh self-suspending proppant (“SSP”)

[00128] A sample of 30/50 mesh size SSP was prepared by adding 500 g of 30/50 frac sand into the bowl of a KitchenAid mixer. 20g of the coating polymer of Example 19 was added to the sand. The mixer was turned on at a setting of 1 and the sand and polymer mixture mixed for 7 minutes. After mixing, the sample was dried for 1 hour at 85°C. After 1 hour, the sample was removed from the oven and any lumps were broken into individual grains.

[00129] Example 22: Reduced fines content of self-suspending proppant (“SSP”) vs. sand

[00130] A stack of standard mesh sieves was prepared with 40 mesh on top, 70 mesh in the middle, and a pan at the bottom. The tare weight of each clean/dry sieve was measured and recorded. 50 g of the 40/70 mesh SSP of Example 20 was added to the top of the sieve stack, and the stack was shaken by hand for five minutes. After shaking, the stack was disassembled and each sieve was weighed. The mass retained on each sieve was calculated as a percent of the original sample mass, and the amount of the sample remaining in the pan represents the fines fraction, as defined by a 70 mesh cutoff. The procedure was repeated, substituting unmodified 40/70 mesh frac sand for the 40/70 SSP. The results in Table 10 show the particle size distribution for 40/70 SSP. Table 11 contains the particle size analysis for unmodified 40/70 frac sand. The results show that the amount of material passing the 70 mesh screen is reduced in 40/70 SSP (1.2% vs. 4.8%). This shows that SSP can contain a reduced amount of fine particulates than a sand sample.

Table 10: Particle size analysis of 40/70 SSP

Sample: 49.516 g of 40/70 SSP

Mesh	Tare, g	Final Mass, g	Mass Sand Retained, g	Size Distribution
40	118.826	127.685	8.859	17.9%
70	111.136	151.036	39.9	80.6%
Pan	81.501	82.072	0.571	1.2%
		Total	49.33	99.6%

Table 11: Particle size analysis of unmodified 40/70 white sand

Sample: 50.974 g of 40/70 White sand

Mesh	Tare, g	Final Mass, g	Mass Sand Retained, g	Size Distribution
40	118.806	118.921	0.115	0.2%
70	111.045	159.465	48.420	95.0%
Pan	81.503	83.935	2.432	4.8%
		Total	50.967	100.0%

5 **[00131]** Example 23: Friction Reduction

[00132] 1 L of tap water was added to a square beaker and the beaker was placed in an EC Engineering CLM-4 Mixer. The mixer was turned on and set to 200 rpm mixing speed. 120 g of the 30/50 SSP of Example 21 was added to the tap water. The slurry mixed for 20 minutes, then was transferred to a 1 L graduated cylinder and left to settle
 10 for 10 minutes. After settling, the supernatant was collected. This procedure was repeated until 2 L of supernatant fluid was collected. The friction reduction of the collected fluid was then determined using a flow loop apparatus. The flow loop consists of a 0.12 in (ID) by 3 ft stainless steel test pipe and a pump that delivers a constant flowrate of 55 gph. These conditions correspond to a Reynolds number of 23,000, confirming that the fluid is
 15 in turbulent flow. The percent friction reduction (%FR) is determined experimentally by measuring the pressures at the entrance and the exit of the test pipe at a constant flow rate. The following equation to calculate the percent friction reduction: $\%FR = 100 * (1 - (\Delta P_i / \Delta P_0))$, where here ΔP_i is the pressure drop across the test pipe using the SSP supernatant fluid and ΔP_0 is the pressure drop across the test pipe using tap water. The
 20 pressure values were $\Delta P_i = 11.8$ psi and $\Delta P_0 = 38.5$ psi, corresponding to a friction

reduction (%FR) of 69%. This shows that the SSP contributes significantly to friction reduction of the associated fluid, representing a reduction in the pumping requirements.

[00133] Example 24: Hydraulic conductivity tests

[00134] To model hydraulic conductivity of a simulated proppant pack, 48 g of 30/50 mesh size SSP of Example 21 were mixed into 1 liter of water. Ammonium persulfate, was added at 0.1% level and the mixture was heated to 185°F for 1 hour. After cooling to room temperature, the mixture was filtered through a 2.25 inch ID column with a 100 mesh sieve at the bottom, separating the particles from the fluid. The particles formed a bed depth of 0.5 inch on the 100 mesh screen, and the flowrates of various fluids through the bed were measured by gravity flow. A plain sand bed was constructed in a similar manner and the flowrates compared with the SSP derived bed. Using this method, the flowrates obtained by SSP (250 mL efflux in 28 seconds) and plain sand (250 mL efflux in 25 seconds) were nearly identical, showing that SSP, once treated with oxidative breakers such as ammonium persulfate, has no deleterious effect on hydraulic conductivity of a sand bed or a simulated proppant pack.

[00135] Example 25: Self-suspending proppants (“SSP”) with anticaking agents

[00136] In addition to anticaking agents being able to replace a drying step, they can be used to generally improve handling qualities for SSP. A number of different particulate materials were tested as anticaking agents, as set forth in Table 12 below. To prepare the samples for each material, 800 g of 30/50 mesh sand was mixed in a KitchenAid mixer at speed 1 (144 rpm) with 32 g of coating polymer of Example 19. 20 g samples were taken and blended with a selected anticaking agent in a mixer, with anticaking agent doses calculated as a percent of the total sand in the sample. The consistency of the samples was observed and recorded as “Appearance before drying,” then they were dried for 1 hour at 85°C. Their consistency was again observed and recorded as “Appearance after drying.” Samples were then subjected to conditions of 80%-90% relative humidity at 25-35°C for one hour to assess their anticaking properties, and consistency was observed and recorded as “Appearance after humidity exposure.” Results are shown in Table 12 below, indicating that the anticaking agent improves the handling properties of the SSP, where free-flowing is a desirable feature.

Table 12: Evaluation of SSP samples with added anticaking agents

Anticaking agent dose	Anticaking agent	Appearance before drying	Appearance after drying	Appearance after humidity exposure
0	None (control)	Wet	Clumpy	Sticky
0.1%	Fumed Silica	Wet	Slightly clumpy	Free-flowing
0.2%	Fumed Silica	Slightly clumpy	Free-flowing	Free-flowing
0.5%	Fumed Silica	Free-flowing	Free-flowing	Free-flowing
0.5%	Calcium Silicate	Free-flowing	Free-flowing	Free-flowing
1%	Corn Starch	Wet	Clumpy	Clumpy
1%	Sodium Stearate	Wet	Clumpy	Slightly clumpy
0.5%	Kaolin	Slightly clumpy	Free-flowing	Free-flowing
0.5%	Bentonite	Slightly clumpy	Free-flowing	Free-flowing
0.2%	Attapulgate	Slightly clumpy	Free-flowing	Free-flowing

[00137] Example 26: Treating Resin Coated Sand with SMA 4000i

[00138] Resin coated sand was coated with SMA 4000i by adding 25 g of resin coated sand into a 250 mL round bottom flask. Separately, 0.25 g of SMA 4000i was dissolved in 3.57 g of tetrahydrofuran (THF) to make a 7% solution. 1.43 g of the THF solution was then added to the resin coated sand in the round bottom flask. Additional THF was added to the round bottom flask until the sand was covered. The THF was then evaporated off of the sample using a rotary evaporator.

10 [00139] Example 27: Treating Resin Coated Sand with SMA 4000i

[00140] Resin coated sand was coated with SMA 2000i by adding 25 g of resin coated sand into a 250 mL round bottom flask. Separately, 0.25 g of SMA 2000i was dissolved in 3.57 g of THF to make a 7% solution. 0.72 g of the THF solution was then added to the resin coated sand in the round bottom flask. Additional THF was added to the round bottom flask until the sand was covered. The THF was then evaporated off of the sample using a rotary evaporator.

[00141] Example 28: Treating Resin Coated Sand with SMA 2000i

[00142] Resin coated sand was coated with SMA 2000i by adding 25 g of resin coated sand into a 250 mL round bottom flask. Separately, 0.25 g of SMA 4000i was dissolved in 3.57 g of THF to make a 7% solution. 1.43 g of the THF solution was then added to the

resin coated sand in the round bottom flask. Additional THF was added to the round bottom flask until the sand was covered. The THF was then evaporated off of the sample using a rotary evaporator.

[00143] Example 29: Treating Resin Coated Sand with SMA 2000i

5 **[00144]** Resin coated sand was coated with SMA 2000i by adding 25 g of resin coated sand into a 250 mL round bottom flask. Separately, 0.25 g of SMA 2000i was dissolved in 3.57 g of THF to make a 7% solution. 0.72 g of the THF solution was then added to the resin coated sand in the round bottom flask. Additional THF was added to the round bottom flask until the sand was covered. The THF was then evaporated off of the sample
10 using a rotary evaporator.

[00145] Example 30: Treating Resin Coated Sand with Pluronic L31

[00146] Resin coated sand was coated with Pluronic Surfactant L31 by adding 20 g of resin coated sand into a small FlackTek jar. 0.025 g of the surfactant was added to the resin coated sand. The sample was then mixed using a FlackTek Speedmixer at 800 rpm
15 for 30 seconds.

[00147] Example 31: Treating Resin Coated Sand with Pluronic L35

[00148] Resin coated sand was coated with Pluronic Surfactant L35 by adding 20 g of resin coated sand into a small FlackTek jar. 0.025 g of the surfactant was added to the resin coated sand. The sample was then mixed using a FlackTek Speedmixer at 800 rpm
20 for 30 seconds.

[00149] Example 32: Treating Resin Coated Sand with Pluronic L81

[00150] Resin coated sand was coated with Pluronic Surfactant L35 by adding 20 g of resin coated sand into a small FlackTek jar. 0.025 g of the surfactant was added to the resin coated sand. The sample was then mixed using a FlackTek Speedmixer at 800 rpm
25 for 30 seconds.

[00151] Example 33: Treating Resin Coated Sand with ARQUAD® 2HT-75

[00152] Resin coated sand was coated with ARQUAD® 2HT-75 by adding 25 g of resin coated sand into a 250 mL round bottom flask. Separately, 0.25 g of ARQUAD® 2HT-75 was dissolved in 3.57 g of IPA to make a 7% solution. 0.72 g of the IPA solution was
30 then added to the resin coated sand in the round bottom flask. Additional IPA was added to the round bottom flask until the sand was covered. The IPA was then evaporated off of the sample using a rotary evaporator.

[00153] Example 34: Treating Resin Coated Sand with ADOGEN® 464

[00154] Resin coated sand was coated with ADOGEN® 464 by adding 20 g of resin coated sand into a small FlackTek jar. 0.025 g of the ADOGEN® 464 was added to the resin coated sand. The sample was then mixed using a FlackTek Speedmixer at 800 rpm
5 for 30 seconds.

[00155] Example 35: Coating Polymer Mixture

[00156] 9 g of Flopam EM 533 (SNF) was combined with 1 g of glycerol in a 20 mL vial. The vial was then mixed for 30 seconds on a vortex mixer.

[00157] Example 36: Hydrogel Coating of Sand Samples

[00158] Sand samples were prepared by placing 20 g of the samples prepared in Example 26 through Example 34 was added to small FlackTek jars. 0.6 g of the coating mixture prepared in Example 35 was added into each the jar. The contents were then mixed at 800 rpm for 1 minute using a FlackTek speed mixer. The samples were then dried for 30 minutes at 100°C. After drying, 1 g of each sample was added to a 20 mL vial containing
10 mL of tap water. The vials were mixed gently then left to settle for 10 minutes. After settling, the bed height was measured to determine polymer hydration. The results of the testing are shown in Table 13.

Table 13: Settled bed heights

Example Number	Additive	Amount on Resin Coated Sand	Bed Height
26	SMA 4000i	4000 ppm	10 mm
27	SMA 4000i	2000 ppm	8 mm
28	SMA 2000i	4000 ppm	8 mm
29	SMA 2000i	2000 ppm	4 mm
30	Pluronic Surfactant L31	1250 ppm	8 mm
31	Pluronic Surfactant L35	1250 ppm	7 mm
32	Pluronic Surfactant L81	1250 ppm	10 mm
33	ARQUAD® 2HT-75	2000 ppm	3 mm
34	ADOGEN® 464	1250 ppm	2 mm

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[00159] Example 37: Humidity Aging Test (Metal Chelate Crosslinkers)

[00160] Tyzor TE is a triethanolamine titanium chelate 80% solution in ethanol. Tyzor TEAZ is a 100% active triethanolamine zirconium chelate product. These metal chelates were dispersed in castor oil at different concentrations and applied to proppant in a second addition step during the coating process. Samples of coated proppant were prepared by adding 3 g of a blend of Flopam EM533 and glycerol to 100 g of 30/50 mesh proppant white sand in a FlackTek Max 100 jar. The samples were then mixed in a FlackTek Speedmixer at 850 rpm for 30 seconds. Samples were then removed from the Speedmixer and in some cases treated with a metal chelate/castor oil blend. Samples were then returned to the Speedmixer and mixed at 850 rpm for 30 seconds. Samples were then removed from the Speedmixer, transferred to a watch glass, and dried at 100°C for 30 minutes in a forced air laboratory oven. After drying, samples were sieved through an 18 mesh screen. For humidity aging, 50 g of the formulated samples were placed in Max 100 FlackTek jars and left sitting in a humidity chamber for 1 hour. The relative humidity of the chamber was kept between 60-70%. After humidification, samples were tested in a Carver Press cell (2.25" I.D.) with an applied load of 1,000 lbs for 30 seconds. Caking of the samples was visually assessed and compared to the control (no second addition). The extent to which samples caked was scored from 1 to 4 with a score of "1" indicating a solid cake and a score of "4" indicating a free-flowing, non-caking material. Results are shown in Table 14.

Table 14 Caking Results with Metal Chelate Add

Sample	Metal chelate	Metal Chelate Conc. (ppm)	Caking Score
1	None	0	1
2	Tyzor TE	600	3
3	Tyzor TE	1500	3
4	Tyzor TEAZ	600	2
5	Tyzor TEAZ	900	3

[00161] (Caking Scores for Table 14: "1"-Solid cake that can be handled without falling apart, "2"-Mostly solid cake that begins to break as handled, "3"-Cake is crumbly out of press cell, "4"-No cake formation).

[00162] Example 38: Humidity Aging Test (Powder Additives)

[00163] Samples of coated proppant sand were formulated by adding 3 g of a Flopam EM533/glycerol blend to 100 g of 30/50 mesh proppant white sand. The samples were mixed at 850 rpm for 30 seconds in a FlackTek Speedmixer. Samples were then removed from the Speedmixer and in some cases treated with a dry powder. Samples were then returned to the Speedmixer and mixed at 850 rpm for 30 seconds to uniformly distribute the powder through the sample. Samples were then removed from the Speedmixer, transferred to a watch glass, and dried at 100°C for 30 minutes in a forced air laboratory oven. After drying, samples were sieved through an 18 mesh screen. For humidity aging about 50 g of the formulated samples were placed in Max 100 FlackTek jars and left sitting in a humidity chamber for 1 hour. The relative humidity of the chamber was kept between 60-70%. After humidification, samples were tested in a Carver Press cell (2.25" I.D.) with an applied load of 1,000 lbs for 30 seconds. Caking of the samples was visually assessed and compared to the control (no second addition). The extent to which samples caked was scored from 1 to 4 with a score of "1" indicating a solid cake and a score of "4" indicating a free-flowing, non-caking material, as shown in Table 15.

Table 15 Caking Results of Coated Proppant with Powder Additive

Sample	Powder	Powder Melting Point (°C)	Powder Conc. (wt%)	Caking Score
6	None	N/A	0.0%	1
7	Thixcin-R	85	0.5%	2
8	Stearic Acid	70	0.6%	3

[00164] (Caking Scores for Table 15: "1"-Solid cake that can be handled without falling apart, "2"-Mostly solid cake that begins to break as handled, "3"-Cake is crumbly out of press cell, "4"-No cake formation).

[00165] Example 39: Oil-based Additives

[00166] Several oil-based or relatively hydrophobic materials were tested to determine their efficacy in decreasing caking in humidified samples of self-suspending proppant (SSP). Samples were prepared by mixing 300 g of 30/50 sand, preheated to 45 °C, with 9 g of a 10% glycerol/90% Flopam 533 mixture in a KitchenAid mixer at speed 1. After 1 minute of mixing, the second additive (usually at 0.2% by wt sand) was introduced and the mixture was mixed for another minute. The sample was dried under medium shear

conditions using a heat gun and KitchenAid. The samples were then subjected to >50% RH in a humidity chamber for 1 hour. They were then individually tested for caking behavior by undergoing the compression test. This consisted of being compressed at 200 PSI for 30 seconds in a compression cell using a Carver Press, then removed from the cell and observed. The resulting cake (See Table 16, Compression Test) was graded on the following scale: “1”-Solid cake that can be handled without falling apart, “2”-Mostly solid cake that begins to break as handled, “3”-Cake is crumbly out of press cell, “4”-No cake formation, as set forth in Table 16.

Table 16 Anti-caking Results of Coated Proppant with Oil Based Additives

2nd Addition: Chemical Identity	2nd Addition: Amount (% of total sand weight)	Compression Test
Control	-	1
Castor Oil	0.2%	1
Triacetin (mixed into polymer)	0.3%	1
Grapeseed Oil	0.2%	1
50% Corn Oil mixed with 50% D400 Jeffamine	0.2%	1
Adogen 464	0.2%	3
50% Adogen 464 mixed with 50% Castor Oil	0.2%	2
10% Adogen 464 mixed with 90% Castor Oil	0.2%	1
Petroleum Jelly	0.2%	1
Mineral Oil (high molecular weight)	0.2%	1
Corn Oil	0.2%	1
Dimethyl, phenylmethyl siloxane, trimethyl terminated	0.2%	1
Aminopropyl terminated poly(dimethyl siloxane)	0.2%	3
50% Adogen mixed with 50% Corn Oil	0.2%	2
Arquad 2HT-75	0.2%	3
Adogen 464	0.1%	3

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[00167] The sample treated with Adogen 464 barely formed a cake in this test, even at lower doses.

EQUIVALENTS

[00168] While specific embodiments of the subject invention have been disclosed herein, the above specification is illustrative and not restrictive. While this invention has been particularly shown and described with references to preferred embodiments thereof, it
5 will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims. Many variations of the invention will become apparent to those of skilled art upon review of this specification. Unless otherwise indicated, all numbers
10 expressing reaction conditions, quantities of ingredients, and so forth, as used in this specification and the claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth herein are approximations that can vary depending upon the desired properties
sought to be obtained by the present invention.

[00169] While this invention has been particularly shown and described with references
15 to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

1. A modified proppant, comprising a proppant particle and a hydrogel coating, wherein the hydrogel coating localizes on the surface of the proppant particle to produce the
5 modified proppant.
2. The modified proppant of claim 1, wherein the proppant particle comprises sand.
3. The modified proppant of claim 1, wherein the proppant particle comprises bauxite,
10 sintered bauxite, ceramic, or lower density materials.
4. The modified proppant of claim 1, wherein the proppant particle comprises a resin-coated substrate.
- 15 5. The modified proppant of claim 4, further comprising an adhesion promoter, wherein the adhesion promoter affixes the hydrogel coating to the resin-coated substrate.
6. The modified proppant of claim 1, wherein the hydrogel coating comprises a water-swallowable polymer.
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7. The modified proppant of claim 1, wherein the hydrogel coating comprises a polymer selected from the group consisting of polyacrylamide, hydrolyzed polyacrylamide, copolymers of acrylamide with ethylenically unsaturated ionic comonomers, copolymers of acrylamide and acrylic acid salts, poly(acrylic acid) or salts thereof, carboxymethyl
25 cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, carboxymethyl guar, carboxymethyl hydroxypropyl guar gum, hydrophobically associating swellable emulsion polymers, and latex polymers.
8. The modified proppant of claim 1, further comprising a cationic/anionic polymer pair
30 comprising a cationic polymer and a high molecular weight anionic polymer.
9. The modified proppant of claim 7, wherein the cationic polymer is selected from the group consisting of poly-DADMAC, LPEI, BPEI, chitosan, and cationic polyacrylamide.

10. The modified proppant of claim 1, further comprising a chemical breaker.
11. The modified proppant of claim 10, wherein the chemical breaker is an oxidative breaker.
- 5 12. The modified proppant of claim 1, further comprising a hydrophobic outer layer.
13. The modified proppant of claim 12, wherein the hydrophobic outer layer is selected from the group consisting of fatty acids, hydrogenated oils, vegetable oils, castor oil, triacetin, waxes, polyethylene oxides, and polypropylene oxides.
- 10 14. The modified proppant of claim 1, further comprising a delayed hydration additive.
- 15 15. The modified proppant of claim 14, wherein the delayed hydration additive is selected from the group consisting of a low hydrophilic-lipophilic balance surfactant, an exclusion agent capable of excluding a finishing surfactant, an ionic crosslinking agent, a covalent crosslinking agent and a monovalent salt charge shielder.
- 20 16. The modified proppant of claim 1, further comprising an alcohol selected from the group consisting of ethylene glycol, propylene glycol, glycerol, propanol, and ethanol.
17. The modified proppant of claim 1, further comprising an anticaking agent.
- 25 18. The modified proppant of claim 1, wherein the hydrogel coating comprises an additive.
19. The modified proppant of claim 18, wherein the additive is a chemical additive.
20. The modified proppant of claim 19, wherein the additive is a tracer.
- 30 21. The modified proppant of claim 19, wherein the additive is a chemical breaker.
22. The modified proppant of claim 1, wherein the modified proppant contains less fines than a proppant particle that is not modified.

23. A hydraulic fracturing formulation, comprising the modified proppant of claim 1.

24. A hydraulic fracturing formulation, comprising the modified proppant of claim 21.

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25. A method of fracturing a well, comprising:

preparing the hydraulic fracturing formulation of claim 23 or claim 24; and

introducing the hydraulic fracturing formulation into the well in an effective

volume and at an effective pressure for hydraulic fracturing,

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thereby fracturing the well.

26. The method of claim 25, comprising:

preparing the hydraulic fracturing formulation of claim 24,

treating the modified proppant with a chemical breaker after the step of

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introducing the hydraulic fracturing formulation into the well.

27. A method of manufacturing a modified proppant, comprising:

providing a proppant substrate particle and a fluid polymeric coating
composition;

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applying the fluid polymeric coating composition on the proppant substrate
particle;

wherein the fluid polymeric coating composition comprises a hydrogel polymer,
and wherein the hydrogel polymer localizes on the surface of the proppant substrate
particle to produce the modified proppant.

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28. The method of claim 27, further comprising the step of drying the modified proppant.

29. The method of claim 27, wherein the manufacturing takes place at or near a point of
use for the modified proppant.

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30. The method of claim 27, wherein the proppant substrate particle comprises sand,
ceramic, low density proppant, a resin coated substrate, and/or bauxite.

31. The method of claim 30, wherein the proppant substrate particle is obtained at or near the point of use for the modified proppant.

32. The method of claim 26, further comprising adding an alcohol selected from the group consisting of ethylene glycol, propylene glycol, glycerol, propanol, and ethanol during or before the step of applying the fluid polymeric coating composition on the proppant substrate particle.

33. The method of claim 27, further comprising adding an inversion promoter during or following the step of mixing the proppant substrate particles and the fluid polymer coating composition.

34. The method of claim 27, further comprising the addition of an anticaking agent to the modified proppant.

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35. A method of manufacturing a hydrogel-coated proppant, comprising:

providing a proppant substrate particle and a formulation comprising a coating precursor, wherein the coating precursor is capable of forming a hydrogel coating on a surface of the proppant substrate particle by *in situ* polymerization;

20 applying the formulation to the proppant substrate particle; and

polymerizing the coating precursor in juxtaposition to the proppant substrate particle to form the hydrogel-coated proppant.

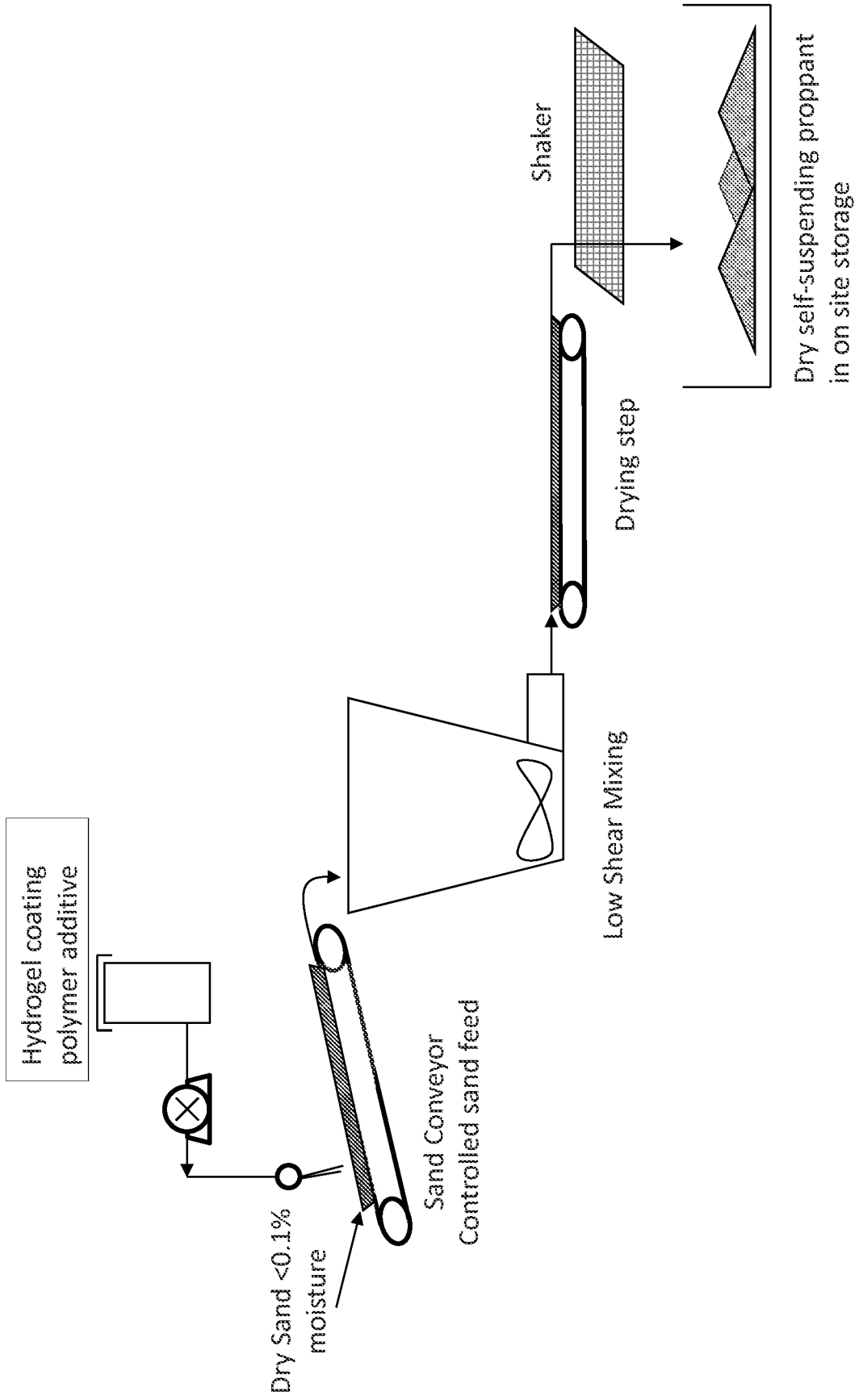


FIG. 1

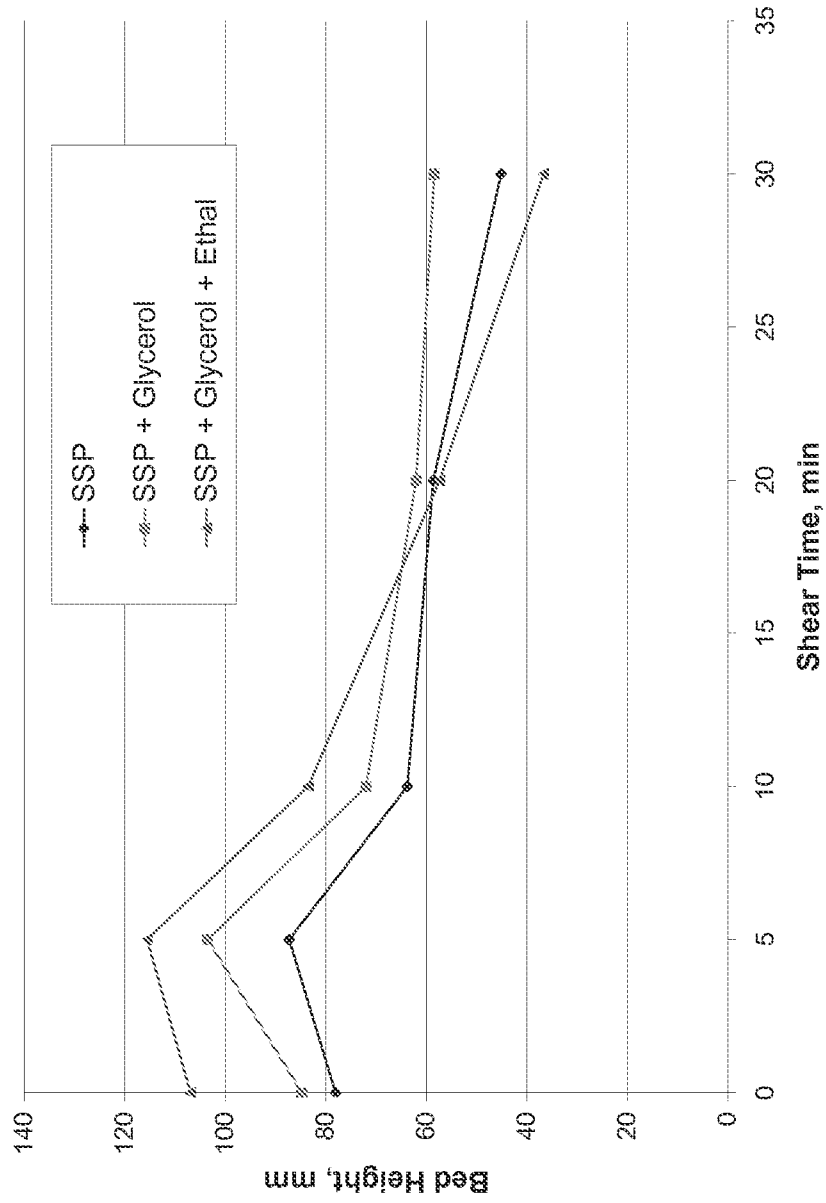


FIG. 2

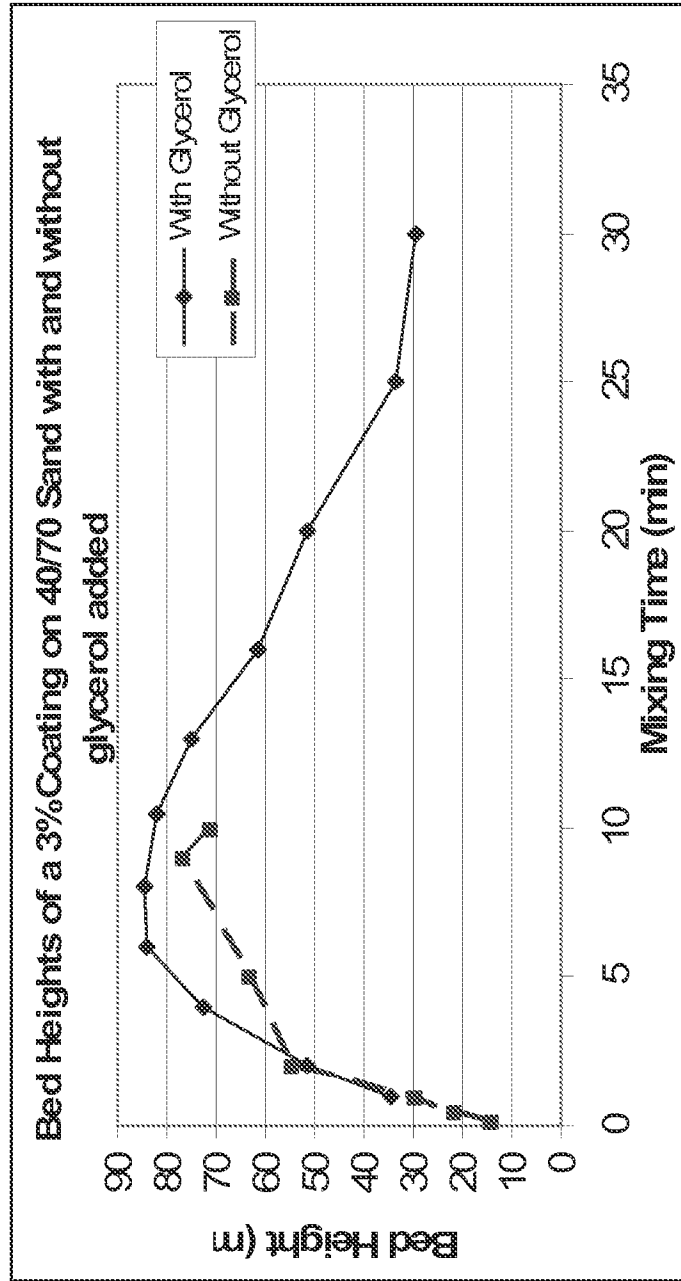


FIG. 3

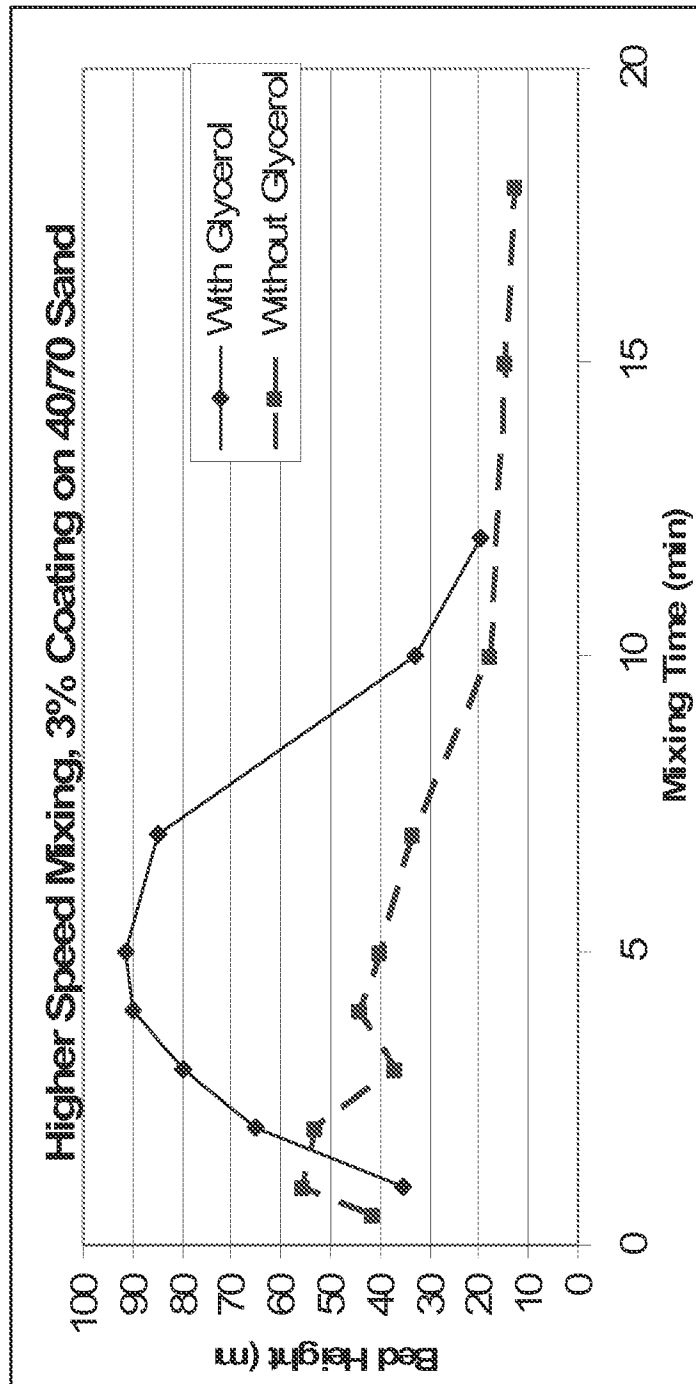


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2013/032435

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09K 8/80 (2013.01)

USPC - 166/280.2

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C09K 8/00, 8/80; E21B 33/00, 33/13, 43/00, 43/25, 43/26, 43/267 (2013.01)

USPC - 166/273, 279, 280.1, 280.2, 293, 308.1; 507/103, 200, 203, 215, 219

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

CPC - C09K 8/00, 8/80, 8/805; E21B 43/26, 43/267 (2013.01)

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

Orbit.com, Google Patents, Public AppFT and PatFT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/0120719 A1 (SOANE et al) 26 May 2011 (26.05.2011) entire document	1-6, 12, 13, 16, 22, 23, 25, 27, 28, 30
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Y		7-11, 14, 15, 17-21, 24, 26, 29, 31, 32, 34
Y	US 2004/0244978 A1 (SHAARPOUR) 09 December 2004 (09.12.2004) entire document	7, 35
Y	US 2010/0249273 A1 (SCALES et al) 30 September 2010 (30.09.2010) entire document	8, 9, 17, 34
Y	US 2008/0289828 A1 (HUTCHINS et al) 27 November 2008 (27.11.2008) entire document	10, 11
Y	US 2008/0108524 A1 (WILLBERG et al) 08 May 2008 (08.05.2008) entire document	14, 15, 18-21, 24, 26, 32
Y	US 7,135,231 B1 (SINCLAIR et al) 14 November 2006 (14.11.2006) entire document	29, 31, 35
Y	US 2005/0274510 A1 (NGUYEN et al) 15 December 2005 (15.12.2005) entire document	20

 Further documents are listed in the continuation of Box C.


* Special categories of cited documents:

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"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

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Date of the actual completion of the international search

20 May 2013

Date of mailing of the international search report

05 JUN 2013

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