



(51) International Patent Classification:

C09K 8/03 (2006.01) *C09K 8/92* (2006.01)
C09K 8/72 (2006.01) *E21B 43/27* (2006.01)
C09K 8/80 (2006.01)

(21) International Application Number:

PCT/US2017/043616

(22) International Filing Date:

25 July 2017 (25.07.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/366,820 26 July 2016 (26.07.2016) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: MICROPARTICLE CARRIERS FOR AQUEOUS COMPOSITIONS AND METHODS OF MAKING

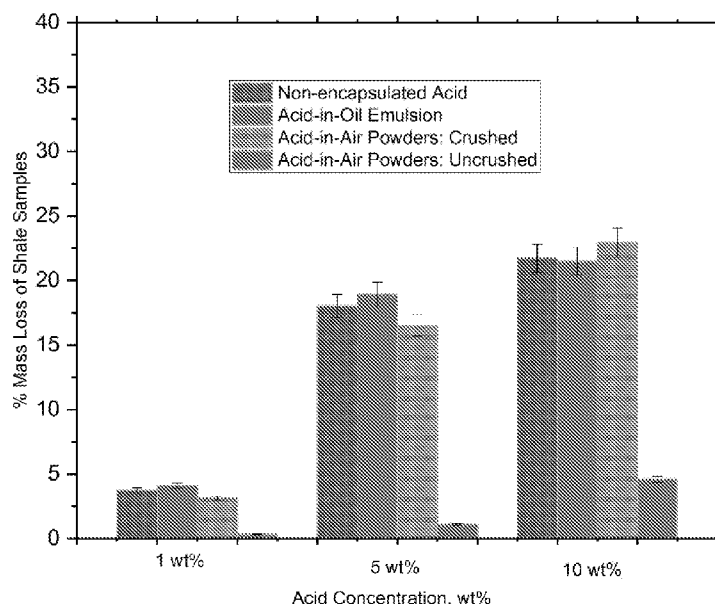


FIG. 3

(57) Abstract: Disclosed herein are microparticles of a hydrophilic liquid encapsulated by hydrophobic nanoparticles. The microparticles are useful in a variety of contexts, including transportation of chemicals, petroleum extraction or recovery, and production of controllably sized resin particles.

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

MICROPARTICLE CARRIERS FOR AQUEOUS COMPOSITIONS AND METHODS OF MAKING

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims the benefit of U.S. Provisional Application 62/366,820, filed July 26, 2016, the contents of which are incorporated in its entirety.

FIELD OF THE INVENTION

10 The invention relates to core/shell microparticles having a hydrophilic core and hydrophobic shell.

BACKGROUND

 Acid fracturing is a technique used to stimulate production in hydrocarbon wells. Typically, a fracture is created in the wellbore, and acid is then introduced into the fracture. The acid then etches channels into the rock along the fracture, increasing the conductivity of the well. Acid fracturing has been successfully employed in shallow, low-temperature carbonate reservoirs. Higher temperature accelerates the reaction with acid, resulting in creation of only short channels. Deep wells are typically characterized by higher temperatures, and also require greater transit times for the acid to reach the fracture. During transit the acid can also be consumed before it reaches the fracture. Even in low-temperature shallow wells, only a small fraction of the acid reaches the fracture.

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 An attempt to overcome the aforementioned difficulties is disclosed in U.S. 6,207,620. This reference proposes the encapsulation of a variety of acid in polymeric systems including natural and synthetic oils, enteric polymers and the like. However, the examples are limited to encapsulation of citric acid. Citric acid, like most other organic acids, are in many cases disfavored for acid fracturing because of their lower reactivity and higher cost. Furthermore, it was later reported that such citric acid systems were especially unsuitable for acid fracturing due to precipitation of calcium citrate salts. More recently the encapsulation of strong acids has been described in U.S. 2016/0017215. There, a hydrophobic monomer (typically a (meth)acrylate) is dispersed in an acidic solution and polymerized, resulting in water-in-oil emulsion, in which the acid solution is encapsulated in a hydrophobic polymer shell.

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 There remains a need for improved methods of acid fracturing. There remains a need for improved methods of selectively delivering acids and proppants to fracture sites within a

well. There remains a need for simple and low-cost methods to encapsulate acids and proppants for use in Enhanced Oil Recovery.

The invention disclosed herein addresses, in part, one or more of the aforementioned needs.

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SUMMARY

Disclosed herein are core/shell microparticles having a hydrophilic liquid core and hydrophobic nanoparticle shell. The core/shell microparticles are useful in a variety of contexts, including Enhanced Oil Recovery (EOR), transportation of hazardous chemicals, and manufacture of controllably sized resin particles.

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The details of one or more embodiments are set forth in the descriptions below. Other features, objects, and advantages will be apparent from the description and from the claims.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 depicts relative emulsion height of acid-in-oil emulsions as a function time at (a) 25 °C, (b) 60 °C, (c) 80 °C; and (d) relative powder height of acid-in-air powders as a function of time for three temperatures.

Figure 2 depicts corrosion rate for different acid systems at (a) 25 °C, (b) 60 °C, and (c) 80 °C.

Figure 3 depicts percentage mass loss of the shale samples for different acid systems with varying acid concentrations.

Figure 4 depicts percentage release of the encapsulated acid from the acid-in-air powders with external aqueous fluid with varying surfactant concentration.

Figure 5 depicts a ternary plot with three axes corresponding to weight fractions of silica nanoparticles, water (20 wt% NaCl) and PPG (2G-110) indicating the final product formed after blending the mixtures under the same operating conditions (a: water axis corresponds to total water; b: water axis corresponds to free water).

Figure 6 depicts percentage release of PPG (2G-110) particles as a function of time with an external aqueous phase of different pH.

Figure 7 depicts percentage release of PPG (2G-110) particles as a function of time with an external aqueous phase of varying surfactant concentrations.

Figure 8 depicts the advancing contact angle of the water droplet with varying pH on a hydrophobic glass slide for time, $t = 0$ and $t = 24$ hours; t_{10} is the time taken to release 10% of particles or ions for different pH cases (secondary y-axis).

Figure 9 depicts the advancing contact angle of the water droplet with varying surfactant concentration on a hydrophobic glass slide for time, $t = 0$ and $t = 24$ hours; t_{10} is the time taken to release 10% of particles or ions for different surfactant concentrations (secondary y-axis).

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DETAILED DESCRIPTION

Before the present methods and systems are disclosed and described, it is to be understood that the methods and systems are not limited to specific synthetic methods, specific components, or to particular compositions. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Ranges may be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

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“Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

Throughout the description and claims of this specification, the word “comprise” and variations of the word, such as “comprising” and “comprises,” means “including but not limited to,” and is not intended to exclude, for example, other additives, components, integers or steps. “Exemplary” means “an example of” and is not intended to convey an indication of a preferred or ideal embodiment. “Such as” is not used in a restrictive sense, but for explanatory purposes.

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Disclosed herein are core-shell microparticles having a hydrophilic core and hydrophobic shell. The microparticles can be a free flowing powder, for instance with an angle of repose of no greater than about 45°, no greater than about 40°, no greater than about 35°, no greater than about 30°, no greater than about 25°, no greater than about 20°, no greater than about 15°, or no greater than about 10°. The microparticles can have an angle of repose

from about 5°-45°, from about 10°-45°, from about 15°-45°, from about 20°-45°, from about 25°-45°, from about 5°-25°, from about 5°-20°, from about 5°-15°, from about 10°-30°, or from about 10°-25°.

The microparticles can be spherical or aspherical. Aspherical microparticles can be
5 characterized by a sphericity number no greater than about 0.95, no greater than about 0.90,
no greater than about 0.85, no greater than about 0.80, no greater than about 0.75, no greater
than about 0.70, no greater than about 0.65, no greater than about 0.60, no greater than about
0.55 or no greater than about 0.50. The microparticles can be characterized by a sphericity
10 number from about 0.50-0.95, about 0.50-0.90, about 0.50-0.85, about 0.50-0.80, about 0.50-
0.75, about 0.50-0.70, or about 0.50-0.65. The sphericity may be expressed as a ratio
between the average minimum length dimension and average maximum length dimension of
the particles (a perfect sphere would have a sphericity of 1)

The microparticles can have an average particle size of about 10,000 μm or less, about
7,500 μm or less, about 5,000 μm or less, about 4,000 μm or less about 3,000 μm or less,
15 about 2,000 μm or less, about 1,250 μm or less, about 1,000 μm or less, about 750 μm or less,
about 500 μm or less, about 400 μm or less, about 300 μm or less, about 200 μm or less,
about 100 μm or less, about 75 μm or less, about 50 μm or less, about 25 μm or less, or about
10 μm or less. In certain embodiments, the microparticles can have an average particle size
of about 10-10,000 μm , 10-7,500 μm , 10-5,000 μm , 100-5,000 μm , 500-5,000 μm , 1,000-
20 5,000 μm , 1,000-2,500 μm , 2,500-10,000 μm , 5,000-10,000 μm , 2,500-7,500 μm , 10-1,000
 μm , about 10-750 μm , about 10-500 μm , about 10-400 μm , about 10-300 μm , about 10-200
 μm , or about 10-100 μm .

The hydrophobic shell can include hydrophobic nanoparticles. The hydrophobic
nanoparticles can have an average particle size less than about 100 nm, less than about 75
25 nm, less than about 50 nm, less than about 40 nm, less than about 30 nm, or less than about
20 nm. In certain embodiments, the hydrophobic nanoparticles can have an average particle
size between about 5-100 nm, between about 5-75 nm, between about 5-50 nm, between
about 5-40 nm, between about 5-30 nm, between about 5-20 nm, between about 10-20 nm, or
between about 15-20 nm.

30 Although the shell can include a variety of different types of hydrophobic
nanoparticles, inorganic nanoparticles are especially preferred. Exemplary inorganic
nanoparticles include particles of Si, Ti, Zn, Al, Sn, Fe, Cu, Zr, B, Mg, Mn, W, Sb, Au, Ag,
Cr, and mixtures thereof. The inorganic nanoparticles can include metal oxide particles such

as zirconia, titania, silica, ceria, alumina, iron oxide, vanadia, zinc oxide, antimony oxide, tin oxide, alumina-silica, and mixtures thereof.

In some embodiments, the hydrophobicity of the nanoparticles can be controlled using surface modifications to the particles. As used herein, surface modification refers to bonding hydrophobic chemical moieties to the surface of the nanoparticles through covalent or ionic bonds, or by partial absorption into the surface of the particle. Exemplary functional groups for bonding include alcohols, amines, carboxylic acids, sulfonic acids, phosphonic acids, silanes, titanates, and the like to give coated hydrophobic nanoparticles. In certain preferred embodiments, the nanoparticles can be treated with silanes, silazanes, or siloxanes (cyclic, dimers, trimers, at the like). Silanes can be preferred for silica and for other siliceous fillers. Silanes and carboxylic acids can be preferred for metal oxides such as zirconia. Exemplary silanes (e.g. organosilanes) include, but are not limited to, alkyltrialkoxysilanes such as n-octyltrimethoxysilane, n-octyltriethoxysilane, isooctyltrimethoxysilane, dodecyltrimethoxysilane, octadecyltrimethoxysilane, propyltrimethoxysilane, and hexyltrimethoxysilane; methacryloxyalkyltrialkoxysilanes or acryloxyalkyltrialkoxysilanes such as 3-methacryloxypropyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, and 3-(methacryloxy)propyltriethoxysilane; methacryloxyalkylalkyldialkoxysilanes or acryloxyalkylalkyldialkoxysilanes such as 3-(methacryloxy)propylmethyldimethoxysilane, and 3-(acryloxypropyl)methyldimethoxysilane; methacryloxyalkyldialkylalkoxysilanes or acryloxyalkyldialkylalkoxysilanes such as 3-(methacryloxy)propyldimethylethoxysilane; mercaptoalkyltrialkoxysilanes such as 3-mercaptopropyltrimethoxysilane; aryltrialkoxysilanes such as styrylethyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, and p-tolyltriethoxysilane; vinyl silanes such as vinylmethyldiacetoxysilane, vinyl dimethylethoxysilane, vinylmethyldiethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, vinyltriisopropoxysilane, vinyltrimethoxysilane, vinyltriphenoxysilane, vinyltri-t-butoxysilane, vinyltris(isobutoxy)silane, vinyltriisopropenoxysilane, and vinyltris(2-methoxyethoxy)silane; and combinations thereof.

The organosilane can include at least one an alkyl group, for instance a C₄₋₃₀ alkyl group, a C₄₋₂₅ alkyl group, a C₄₋₂₀ alkyl group, a C₈₋₂₀ alkyl group, or a C₁₀₋₂₀ alkyl group. The term alkyl group, unless specified to the contrary, includes linear, branched or cyclic groups, fully saturated alkyl groups, partially unsaturated alkyl groups, and full unsaturated alkyl group. As used herein, fully saturated mean there are no carbon-carbon double or triple bonds present. Partially saturated means that there is at least one carbon-carbon double or

triple bond, and at least one sp^3 hybridized carbon atom. Fully saturated means that there are no sp^3 hybridized carbon atoms. In some instances, linear alkyl groups are preferred. In other embodiments, the organosilane can have the formula $-SiR_3$, wherein R is independently selected from $-R^a$ or OR^a , wherein R^a is independently selected from C_{1-30} alkyl. Non-
5 limiting examples of alkyl groups include butyl, iso-butyl, sec-butyl, pentyl, iso-pentyl, neo-pentyl, hexyl, 2-ethylhexyl, octyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, octadecyl, cyclohexyl, 4-methylcyclohexyl, cyclohexylmethyl, cyclopentyl, and cyclooctyl. The alkyl group may optionally comprise other substituents.

Carboxylic acid surface modifying agents may comprise the reaction product of
10 phthalic anhydride with an organic compound having a hydroxyl group. Suitable examples include, for example, phthalic acid mono-(2-phenylsulfanyl-ethyl)ester, phthalic acid mono-(2-phenoxy-ethyl)ester, or phthalic acid mono-[2-(2-methoxy-ethoxy)-ethyl]ester. In some examples, the organic compound having a hydroxyl group is a hydroxyl alkyl(meth)acrylate such as hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, or
15 hydroxybutyl(meth)acrylate. Examples include, but are not limited to, succinic acid mono-(2-acryloyloxy-ethyl)ester, maleic acid mono-(2-acryloyloxy-ethyl)ester, glutaric acid mono-(2-acryloyloxy-ethyl)ester, phthalic acid mono-(2-acryloyloxy-ethyl)ester, and phthalic acid mono-(2-acryloyl-butyl)ester. Still others include mono-(meth)acryloxy polyethylene glycol succinate and the analogous materials made from maleic anhydride glutaric anhydride, and
20 phthalic anhydride.

The surface treatment may comprise a blend of two or more hydrophobic surface treatments. For example, the surface treatment may comprise at least one surface treatment having a relatively long substituted or unsubstituted hydrocarbon group. In some
embodiments, the surface treatment comprises at least one hydrocarbon group having at least
25 6 or 8 carbon atoms, such as isooctyltrimethoxy silane, with a second surface treatment that is less hydrophobic, such as methyl trimethoxy silane.

In certain embodiments, a monolayer of surface modifier is present on nanoparticles. In some embodiments, the monolayer is present wherein at least 80%, 85%, 90%, 92.5%, 95%, 97.5% or 99% of the reactive sites on the surface of the nanoparticles are bound to the
30 modifier.

The surface modification of the nanoparticles in the colloidal dispersion can be accomplished in a variety of ways. The process involves the mixture of an inorganic dispersion with surface modifying agents. Optionally, a co-solvent can be added at this point, such as for example, 1-methoxy-2-propanol, methanol, ethanol, isopropanol, ethylene glycol,

N,N-dimethylacetamide, 1-methyl-2-pyrrolidinone, and mixtures thereof. The co-solvent can enhance the solubility of the surface modifying agents as well as the dispersibility of the surface modified nanoparticles. The mixture comprising the inorganic sol and surface modifying agents is subsequently reacted at room or an elevated temperature, with or without
5 mixing.

The hydrophilic core can include a hydrophilic liquid, for instance water, polar organic solvents, and mixtures thereof. Exemplary polar organic solvents include lower alcohols like methanol, ethanol, isopropanol and n-propanol, carbonyl and sulfoxide compounds like acetone, DMSO, or DMF. The hydrophilic core can include any one or more
10 of acids, bases, salts, polymers, wetting agents, gelling agents and mixture thereof. The hydrophilic liquid can be a solution or dispersion.

Compared with some core-shell microparticles, the disclosed microparticles can have a much higher concentration of hydrophilic liquid relative to the hydrophobic nanoparticles. For instance, the hydrophilic liquid can be present in the microparticles in an amount of at
15 least 50%, at least 60%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 92.5%, at least 95%, at least 97.5%, at least 99%, or at least 99.5%, by weight of the total microparticles. In some embodiments, the ratio (wt/wt) of the hydrophilic liquid to hydrophobic nanoparticles can be at least 2:1, at least 3:1, at least 4:1, at least 5:1, at least
20 6:1, at least 7:1, at least 8:1, at least 9:1, at least 10:1, at least 12.5:1, at least 15:1, at least 17.5:1, at least 20:1, at least 25:1, at least 30:1, or at least 50:1. In some embodiments, the ratio (wt/wt) of the hydrophilic liquid to hydrophobic nanoparticles can be from 2:1 to 50:1, from 3:1 to 50:1, from 4:1 to 50:1, from 5:1 to 50:1, from 5:1 to 40:1, from 5:1 to 30:1, from 10:1 to 50:1, from 10:1 to 30:1, or from 10:1 to 25:1.

In certain embodiments, the hydrophilic is a liquid having a pH of less than about 7,
25 less than about 6, less than about 5, less than about 4, less than about 3, less than about 2, or less than about 1. In some embodiments, the hydrophilic liquid can have a pH from about 1-7, about 2-6, about 2-5, or about 3-5. The hydrophilic liquid can include one or more organic acids, inorganic acids, and mixtures thereof. Suitable organic acids include formic acid, acetic acid, oxalic acid, tartaric acid, maleic acid, succinic acid, fumaric acid, citric acid,
30 glyoxylic acid, lactic acid, pyruvic acid, propionic acid, chloroacetic acid, trichloroacetic acid, trifluoroacetic acid, butyric acid, toluenesulfonic acid, methanesulfonic acid, trifluoromethane sulfonic acid, and mixtures thereof. Suitable inorganic acids include hydrochloric acid, hydrofluoric acid, hydrobromic acid, hydroiodic acid, nitric acid, boric acid, perchloric acid, sulfuric acid, phosphoric acid, and mixtures thereof.

In some embodiments, the hydrophilic liquid includes one or more salts. Suitable salts include alkaline and alkaline earth salts such as lithium chloride, lithium bromide, sodium chloride, sodium bromide, calcium chloride, magnesium chloride, potassium chloride and the like. The salt can be present in an amount of at least 1 wt%, at least 2.5 wt%, at least 5.0 wt%, at least 7.5 wt%, at least 10 wt%, at least 12.5 wt%, at least 15 wt%, at least 17.5 wt%, at least 20 wt%, at least 25 wt%, or at least 30 wt%, relative to the total weight of the microparticles.

In certain embodiments, the hydrophilic liquid includes one or more gelling agents. Suitable gelling agents include polyacrylamide, polyacrylic acid-polyacrylamide copolymers, curdlan and the like. The gelling agent can be present in an amount of at least about 1%, at least about 2.5%, at least about 5%, at least about 7.5%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 40%, at least about 45%, or at least about 50% (w/w) relative to the total weight of the core-shell microparticles.

In some embodiments, the core-shell microparticles can include superparamagnetic particles. The superparamagnetic particles can be used to selectively rupture the microparticles at the desired time and location. The superparamagnetic particles can be present in an amount of at least 0.01%, 0.05%, 0.10%, 0.15%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% or 0.50% by weight, relative to the total weight of the core-shell microparticles. In some instances, the ratio of the hydrophobic nanoparticles to superparamagnetic particles can be from about 10,000:1 to 50:1, about 5,000:1 to 50:1, about 2,500:1 to 50:1, about 1,000:1 to 50:1, about 500:1 to 50:1, about 250:1 to 50:1, or about 100:1 to 50:1. The superparamagnetic particles can be in the hydrophilic core, in the hydrophobic shell, or both. The use of hydrophobic superparamagnetic particles results in the particles in the shell, whereas use of hydrophilic superparamagnetic particles results in the particles in the core. While most superparamagnetic nanoparticles are naturally hydrophilic, they can be coated with silicon dioxide and the surface functionalized to render them hydrophobic. Exemplary superparamagnetic particles include magnetite, maghemite, nickel or cobalt.

The core-shell microparticles can be characterized by greater stability relative to conventional microparticles. For instance, the microparticles can retain their core-shell shape such that there is no leakage of hydrophilic liquid (e.g., phase separation) when the particles are stored under ambient conditions. Under some embodiments, the core-shell microparticles only begin to leak under pressure and temperatures greater than 80° C.

The core-shell microparticles disclosed herein can be prepared by agitating a mixture of hydrophobic nanoparticles and hydrophilic liquid. The hydrophobic nanoparticles and hydrophilic liquid can be combined at levels and ratios described above. For instance, the hydrophilic liquid can be combined with the hydrophobic nanoparticles in an amount of at least 50%, at least 60%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 92.5%, at least 95%, at least 97.5%, at least 99%, or at least 99.5%, by weight of the total mixture. In some embodiments, the components can be combined in a ratio (wt/wt) of the hydrophilic liquid to hydrophobic nanoparticles of at least 2:1, at least 3:1, at least 4:1, at least 5:1, at least 6:1, at least 7:1, at least 8:1, at least 9:1, at least 10:1, at least 12.5:1, at least 15:1, at least 17.5:1, at least 20:1, at least 25:1, at least 30:1, or at least 50:1. In some embodiments, the components can be combined in a ratio (wt/wt) of the hydrophilic liquid to hydrophobic nanoparticles from 2:1 to 50:1, from 3:1 to 50:1, from 4:1 to 50:1, from 5:1 to 50:1, from 5:1 to 40:1, from 5:1 to 30:1, from 10:1 to 50:1, from 10:1 to 30:1, or from 10:1 to 25:1.

The superparamagnetic particles may be combined with hydrophilic liquid prior to introducing the hydrophobic nanoparticles. In some embodiments, the components can be combined and then agitated, while in others, the components can be combined under agitation. For instance, the hydrophobic nanoparticles can be added to the hydrophilic liquid while the liquid is being agitated. The addition can take place over 1 minute, over 5 minutes, over 10 minutes, over 30 minutes, over 60 minutes, over 120 minutes, over 240 minutes, over 360 minutes, or over 480 minutes. In some instances, the hydrophobic nanoparticles can be combined with superparamagnetic particles and then the blend can be gradually added to the hydrophilic liquid. The hydrophilic liquid can be combined with superparamagnetic particles and then combined with the hydrophobic nanoparticles under agitation. The hydrophilic liquid, superparamagnetic particles, and hydrophobic nanoparticles can be combined together, and the mixture then agitated.

In some instances, the agitating can include stirring. The stirring rate can be at least 1000 rpm, at least 2000 rpm, at least 3000 rpm, at least 4000 rpm, at least 5000 rpm, at least 6000 rpm, at least 7000 rpm, at least 8000 rpm, at least 9000 rpm, at least 10,000 rpm, at least 10,000 rpm, at least 10,000 rpm, at least 10,000 rpm, at least 15,000 rpm, at least 20,000 rpm, at least 15,000 rpm, at least 20,000 rpm, at least 25,000 rpm, at least 30,000 rpm, at least 35,000 rpm, or at least 40,000. The stirring is conducted until the mixture has become a free flowing powder, with no detectable hydrophilic liquid remaining.

The core/shell microparticles can be dispersed in an oil to form an emulsion. Traditional water-in-oil emulsions require the presence of surfactant to stabilize the hydrophilic droplets in the oil phase. The disclosed emulsions, on the other hand, can be prepared without added surfactant because the microparticles will not coalesce in the oil phase. As such, emulsions containing the disclosed microparticles, including those that do not have added surfactant, are more stable than conventional water-in-oil emulsions. Emulsion stability can be measured in half-life, in the amount of time it takes the water droplets to coalesce. Conventional water-in-oil emulsions have half-lives measured in hours, whereas emulsions prepared with the microparticles disclosed herein have essentially an infinite half-life, meaning that at no point do the particles and/or hydrophilic liquid begin to coalesce.

In some embodiments, the emulsions can include an oil selected from alkane hydrocarbons, mineral oils, diesel, crude oils and mixtures thereof. [The microparticles can be present in an amount of at least 2%, 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, or 75% (w/w) relative to the total weight of the emulsion.

The microparticles can be obtained by combining the nanoparticles and hydrophilic liquid under conditions sufficient to obtain the microparticles. In some instances, the mixture may be agitated with sufficient energy to give the nanoparticles. A hydrophobic liquid, for instance an oil, may also be included. Such a process can directly yield an emulsion of microparticles. Generally, the higher the level of agitation energy, the smaller the particle size of microparticles. The agitating can include stirring, for instance stirring a rate of at least 1000 rpm, at least 2000 rpm, at least 3000 rpm, at least 4000 rpm, at least 5000 rpm, at least 6000 rpm, at least 7000 rpm, at least 8000 rpm, at least 9000 rpm, at least 10,000 rpm, at least 15,000 rpm, at least 20,000 rpm, at least 25,000 rpm, at least 30,000 rpm, at least 35,000 rpm, at least 40,000 rpm, at least 45,000 rpm, or at least 50,000 rpm.

In other embodiments, the microparticles can be obtained by passing a mixture of hydrophobic nanoparticles and hydrophilic liquid through a filter under pressure sufficient to obtain the microparticles. The filter can have a pore size between 1-500 microns, between 10-500 microns, between 25-500 microns, between 50-500 microns, between 50-400 microns, between 50-300 microns, between 50-250 microns, between 75-250 microns, between 100-250 microns, or between 100-200 microns. The pressure applied to force the mixture through the filter can be at least 10 psi, at least 25 psi, at least 50 psi, at least 75 psi, at least 100 psi, at least 150 psi, at least 200 psi, at least 250 psi, or at least 300 psi.

The microparticles can be used to selectively deliver the hydrophilic liquid to a location in a well. Generally, the microparticles (or microparticle emulsion) can be combined with a carrier and then pumped downwell. The carrier can include gases such as CO₂ or hydrocarbons, or hydrophilic liquids like crude oil, decane, vegetable oil, diesel, and the like.

5 The particles can be selectively ruptured to deliver the hydrophilic liquid at the desired location.

Microparticles that contain superparamagnetic particles can be selectively ruptured by magnetic induction. An oscillating magnetic field will heat the particles causing the hydrophobic shell to break apart. In some embodiments the microparticles can be pumped
10 downwell under pressure, during hydraulic fracturing, refracturing or stimulation. This pressure enlarges and/or creates fractures, in which the microparticles can become lodged. When the pressure is reduced, the fractures shrink, squeezing the microparticles and causing them to rupture. The rupturing can release chemicals such as acids from the microparticles. In some instances, microparticles can be ruptured by introducing surfactant systems down
15 well. Many surfactants (anionic, nonionic, cationic or zwitterionic) can be used. Exemplary surfactant systems include alkyl sulfonates, alkyl benzene sulfonates, alkyl ethoxylates, Amphoam, sodium dodecyl sulfate, and cetyltrimethylammonium bromide.

The microparticles can be delivered at various stages of wellbore operation, for instance during initial fracturing, refracturing, huff-and-puff periods, and combinations
20 thereof. The microparticles can be delivered at a variety of densities, for instance in at least about 1 g/ft², at least about 5 g/ft², at least about 10 g/ft², at least about 25 g/ft², at least about 50 g/ft², at least about 75 g/ft², at least about 100 g/ft², at least about 125 g/ft², at least about 150 g/ft², or at least about 200 g/ft² can be delivered to the fracture surface. In certain
25 embodiments, about 1-200 g/ft², about 5-200 g/ft², about 10-200 g/ft², about 25-200 g/ft², about 50-200 g/ft², about 50-150 g/ft², about 75-125 g/ft², or about 100 g/ft² can be delivered to the fracture surface, calculated based on the amount of particles injected divided by the area of fracture created.

In some embodiments, the microparticles can be used to controllably prepare resin particles of uniform size. One or more polymerizable monomers can be dispersed or
30 dissolved in a hydrophilic liquid and converted into core/shell microparticles using the techniques described herein. The nanoparticles can then be subject to conditions sufficient to polymerize the monomer, after which the hydrophobic core can be removed and the resin particles recovered. The obtained resin particles can be uniform in size and shape, e.g., monodisperse. Exemplary polymerizable monomers include ethylenically unsaturated

compounds, such as vinyl compounds, dienes, α,β -monoethylenically unsaturated mono- and dicarboxylic acids, and esters, amides or anhydrides thereof. Exemplary α,β -monoethylenically unsaturated mono- and dicarboxylic acids include (meth)acrylic acid, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, amyl(meth)acrylate, isobutyl(meth)acrylate, t-butyl(meth)acrylate, pentyl(meth)acrylate, isoamyl(meth)acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate, octyl(meth)acrylate, isooctyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, nonyl(meth)acrylate, decyl(meth)acrylate, isodecyl(meth)acrylate, undecyl(meth)acrylate, dodecyl(meth)acrylate, lauryl(meth)acrylate, octadecyl(meth)acrylate, stearyl(meth)acrylate, tetrahydrofurfuryl(meth)acrylate, butoxyethyl(meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl(meth)acrylate, cyclohexyl(meth)acrylate, phenoxyethyl(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethoxyethyl(meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, dicyclopentadiene(meth)acrylate, dicyclopentanyl(meth)acrylate, tricyclodecanyl(meth)acrylate, isobornyl(meth)acrylate, bornyl(meth)acrylate. Similar esters may be derived using fumaric acid and itaconic acid as well.

The hydrophilic liquid can also include a free-radical initiator, for instance one or more of alkali metal peroxydisulfates H_2O_2 , azo compounds. Combined systems can also be used comprising at least one organic reducing agent and at least one peroxide and/or hydroperoxide, e.g., *tert*-butyl hydroperoxide and the sodium metal salt of hydroxymethanesulfinic acid or hydrogen peroxide and ascorbic acid.

Disclosed are components that can be used to perform the disclosed methods and systems. These and other components are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these components are disclosed that while specific reference of each various individual and collective combinations and permutation of these may not be explicitly disclosed, each is specifically contemplated and described herein, for all methods and systems. This applies to all aspects of this application including, but not limited to, steps in disclosed methods. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the disclosed methods.

EXAMPLES

The following examples are set forth below to illustrate the methods and results according to the disclosed subject matter. These examples are not intended to be inclusive of all aspects of the subject matter disclosed herein, but rather to illustrate representative
5 methods, compositions, and results. These examples are not intended to exclude equivalents and variations of the present invention, which are apparent to one skilled in the art.

Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and
10 pressure is at or near atmospheric. There are numerous variations and combinations of reaction conditions, e.g., component concentrations, temperatures, pressures, and other reaction ranges and conditions that can be used to optimize the product purity and yield obtained from the described process. Only reasonable and routine experimentation will be required to optimize such process conditions.

Example 1a: Encapsulation of acetic acid

Highly hydrophobic nanoparticles of 20-30 nm diameter were stirred with mixed in 5 wt% acetic acid. The mixture was kept inside a blender and blended for a minute under a speed of about 16000 rpm whereby dry particles were obtained encapsulating acetic acid.
20 The ratio of nanoparticles to liquid was 1:12 by weight for this example.

Example 1b: Encapsulation of hydrochloric acid

Hydrophobic silica nanoparticles and aqueous hydrochloric acid solution (1 wt%) were placed in a blender (Bella-Rocket blender) in a ratio of 1:10 by weight. The volume of the blending cup was 350 cc. The mixture was blended at constant speed of 16000 rpm for 60
25 seconds using a cross-blade attachment. It resulted in the formation of water-in-air (or acid-in-air) powders with hydrochloric acid solution completely encapsulated inside the silica shell. Similar particles were obtained from 5 wt% and 10 wt% HCl solutions

Example 2: Formation of acid-in-oil emulsion

Concentrated acid (5 wt% HCl) with 1 wt% Tergitol surfactant and decane were taken
30 in a vial in the ratio of 70:30. A small amount of hydrophilic dye, Nile Blue A was added to the aqueous acid phase for visualization purpose. The mixture was mixed vigorously using a homogenizer (Ultra-Turrax T25) operating at 10000 rpm for 30 seconds. It resulted in the formation of the acid-in-oil emulsion. Similar emulsions were prepared using 50:50 and 90:10 ratios.

Example 3: Heat stability

The thermal stability of both acid-in-oil emulsion and the acid-in-air powder was assessed at 25, 60, and 80 °C. The acid concentration was kept constant at 5 wt%. The stability of the emulsion was measured in terms of relative emulsion height as a function of time. Relative emulsion height is the ratio of height (or volume) to the initial emulsion height just after mixing. A higher emulsion height indicates slower release of acid via bubble coalescence. The half-life ($t_{1/2}$) of the emulsion, a measure of bulk emulsion stability, can be defined as the time taken for the emulsion to break to half of its original height. Analogous to the emulsions, the stability of these powders was evaluated based on the relative powder height (or volume) with time. To quantify the released acid accurately and ensure there is no trapped released acid in the powders, the particles were taken out of the ovens intermittently and were centrifuged at 3000 rpm for 3 minutes. As shown in the following table, acid-in-air particles are substantially more stable than emulsions, especially at higher temperatures. At each temperature, the particles never reached half-height over the course of the experiment (200 hours). The number in parenthesis reflect the relative height of the particles after 200 hours compared with the initial height (Figure 1):

Temp.	Time to half-height			
	50:50 emul.	70:30 emul.	90:10 emul.	Particles
25°	$t_{1/2} = >180$ h	$t_{1/2} < 2.5$ h	$t_{1/2} < 2.5$ h	$t_{1/2} = > 200$ h (94.5%)
60°	$t_{1/2} = 1.3$ h	$t_{1/2} = 2.7$ h	$t_{1/2} = 0.5$ h	$t_{1/2} = > 200$ h (83.5%)
80°	$t_{1/2} = 0.9$ h	$t_{1/2} = 1.2$ h	$t_{1/2} = 0.4$ h	$t_{1/2} = > 200$ h (84.0%)

Example 4: Corrosion study

The experiment was conducted at 60 °C, at acid concentrations of 1, 5, and 10 wt%. In the first case, iron samples were submerged in acid directly (referred here as non-encapsulated acid) and were placed in the oven for a fixed amount of time. In the second case, the iron samples were placed in the acid-in-oil emulsions (50:50). Finally, in the third case, the iron samples were placed in the acid-in-air powders. The total amount of acid was kept constant in all three cases. At every temperature, highest corrosion rate was found for the non-encapsulated acid. The corrosion rate was relatively reduced for the case of acid-in-oil emulsions for all the cases, and was reduced to a substantially greater degree for the acid-

in-air particles (Figure 2). For example, the corrosion rate for the acid-in-oil emulsion was reduced from 3121.9 mm.y-1 to 136.8 mm.y-1 (reduction factor of 22.82) for the case of 5 wt% acid concentration at 60 °C, whereas for the acid-in-air particles the corrosion rate was only 31.6 mm.y-1 (reduction factor of 98.79).

5 **Example 5: Pressure-induced release of encapsulated acid**

Experiments were performed at 60°C and reaction period was 24 hours for each case. Three different HCl concentrations (1, 5, 10 wt%) were used. Since the permeability of the shale samples is very low, the acid reaction will be strongly governed by the surface area. Therefore, all the shale samples were cut in similar size and shape to ensure same surface
10 area. The shale samples were contacted with the following systems at 60° C for 24 hours:
(1) non-encapsulated acid (1, 5, and 10 wt%);
(2) acid-in-oil emulsions (1, 5, and 10 wt%), acid solution:water 1:1;
(3) acid-in-air particles; and
(4) crushed acid-in-air particles (obtained by pressing the entire system using a Teflon-coated
15 plate to crush the acid powders (to mimic the fracture closure).

As shown in Figure 3, the amount of shale lost when contacted with non-encapsulated acid was very similar to that when shale was contacted with acid-in-oil emulsions. On the other hand, hardly any shale was lost in the case of acid-in-air particles. Finally, when the particles were crushed in the presence of shale, the amount of shale lost was very similar to
20 that observed with non-encapsulated acid.

This experiment shows that how acid-in-air powders can act as carrier agents for concentrated acid. The reaction of acids with shale surface would be considerably retarded when no external stimuli such as mechanical pressure were applied. The fracture closure will result in the instant release of acid which will result in surface-etching and increased fracture
25 conductivity post-fracture closure.

Example 6: Surfactant-induced release of encapsulated acid

An alternative strategy for the controlled-release is possible using the addition of surfactants to the carrier fluid transporting the powders. Acid-in-air powders were mixed
30 with an aqueous solution with varying concentration of the amphoteric surfactant and the vials were placed in the oven operating at 60 °C. A small amount of aqueous sample was taken intermittently to measure the amount of release chloride ions using ion chromatography which gives the measure of the amount of acid released with time. Figure 4 shows the plot of

the percentage release of acids with time. The total amount of acid released was normalized using the maximum amount of acid present in the system. For the case of 1 wt% surfactant all the encapsulated acid was instantly released. The t_{50} , time taken for the 50% of acid to release, was 3.5, 438.2, 3625.6, and 4146.7 minutes. The degree of acid release was reduced
5 with a reduction in the surfactant concentration.

Example 7: Encapsulation of gelling agent

Commercially available, salinity-sensitive super-absorbing material or preformed particle gel (PPG) with tradename LiquiBlock™ 2G-110 was supplied by Emerging
10 Technologies. Hydrophobic silica nanoparticles, Aerosil R 202 were obtained from Evonik Industries. These nanoparticles are 14 nm in size and are coated with polydimethylsiloxane. Zwitterionic surfactant, Amphoam was supplied by Weatherford. Sodium Chloride (Fisher) was used as received.

High salinity water (20 wt% NaCl) and PPG micro-particles (size < 600 micron) were
15 mixed in the ratio of 5:1 by weight. These particles were fairly dispersible in water. The presence of such high concentration of sodium chloride inhibits the swelling of the particles. Second, this dispersed PPG micro-particles and hydrophobic nanoparticles were taken in a mixer in the ratio of 12:1 by weight. Finally, the mixer was operated at 4000 rpm for about 2 minutes allowing rigorous mixing. The final product is a water-in-air emulsion, i.e., saline
20 water containing un-swelled PPG particles surrounded by silica nanoparticles. The final product behaved like a powder in terms of appearance and flow behavior in glass vials.

The obtained dry-water is then mixed with low-salinity water in the ratio of 1:14.62 by weight. This mixture was mixed in a plastic vial and was shook vigorously. The final product was dry-water fairly well-dispersed in water. No phase separation was observed even
25 after several days (> 5day). Different pumps such as ISCO syringe pump (Teledyne, NE), Masterflex Peristaltic pump (Cole-Parmer, IL), and Quizix Pump (Chandler Engineering, OK) were tested in the labs to pump it. No phase separation was observed after pumping the mixture through tubes suggested it can be pumped effectively.

The microparticles were then mixed with Amphoam (0.01 wt%, 0.1 wt% and 0.5
30 wt%). The vials were placed on tube shaker (LabQuake, Thermo Scientific) and the macroscopic fluid flow behavior was observed. It was observed that particles were completely swelled after 4 days, 4.5 days and 6 hours, respectively for these three cases. As the surfactant adsorbs into the shell, the shell becomes more hydrophilic and susceptible to rupture in aqueous environments. Shell rupture releases the un-swelled PPG dispersed in high

saline water to low salinity water. Once the sodium chloride concentration is diluted, the PPG particles starts adsorbing water resulting in swelling of these particles. The swelling ratio (ratio of final particle size to initial particle size) was as high as 150 depending on final salinity.

5 **Example 8: Encapsulation of gelling agent**

5 grams of PPG (LiquiBlock™ 2G-110) was dispersed in 25 grams of 20 wt% NaCl solution. The PPG instantly absorbs the water and forms a gel. This gel was placed in a blending cup and was mixed with 2.5 gm of hydrophobic silica nanoparticles at 16,000 rpm for 1 minute. It resulted in formation of dry powders (termed encapsulated PPG powder, EPP) which flow freely through glass funnels as opposed to a gel which does not flow without application of a shear force. The weight ratio of nanoparticles to water (20 wt% NaCl) to PPG was 1:10:2. The free water (non-absorbed water) in this case was zero.

The particle size was calculated to be 39 ± 25 microns by analyzing at least 200 particles. An irregularly shaped surface morphology of the EPP is obtained. Since the amount of free water in this case was zero, the inner core of the EPP was expected to be only PPG particles. A CLSM analysis of another sample was then performed in which very less PPG particles are present. A ratio of nanoparticles to water (20 wt% NaCl) to PPG = 1:10:0.05 was chosen.

To validate that all the PPG (2G-110) micro-particles were completely encapsulated by the silica nanoparticles, 0.8 gm of encapsulated PPG powder (EPP) was mixed with 39.2 gm deionized (DI) water in a centrifuge tube. The sample was vigorously hand shaken for 1 minute and then placed on LabQuake® shaker (Barnstead Thermolyne) at the room temperature for agitation for 24 hours. The sample was then centrifuged in a CRU-5000 centrifuge (Damon/IEC Division) operating at 3000 rpm for 2 minutes. No precipitate of PPG was observed indicating complete encapsulation of PPG micro-particles inside the silica nanoparticle protective coating. Note that PPG swells in the presence of DI water. The coating protects the PPG particles completely from the outside low-salinity water, and thus preventing any swelling.

Assuming homogenous PPG (2G-110) concentration (by mass) inside the EPP powder, 0.8 gm of EPP corresponds to 0.123 gm of PPG (2G-110). If the encapsulation completely breaks, the final salinity of the solution would be 0.31 wt%. The total expected swelling ratio at this salinity is 101 as reported in the Supporting Information (Table S1). The silica nanoparticles used in the present study are highly dispersible in ethanol. To instantly break the encapsulation, 5 gm of ethanol was then added to the sample and was mixed

vigorously. The sample was again centrifuged and swollen PPG was observed in the precipitate. The swelling ratio came out to be 101, exactly as would be expected. This procedure was repeated several times and the result was repeatable with an error of 0.8% which shows that PPG concentration in the EPP is quite homogenous. In a similar way, the second type of PPG (LiquiBlock™ 40F) was successfully encapsulated and a free-flowing Encapsulated PPG Powder (EPP) was obtained.

In the above cases, the weight ratio of nanoparticles to water (20 wt% NaCl) to PPG (2G-110) was 1:10:2 by weight. The ratio of nanoparticles to water (20 wt% NaCl) to PPG (2G-110) was then varied from 1:1:0 to 1:60:16 to fully-identify the domain of the possible ratios, where EPP can be formed. These mixtures with varying ratios were blended under the same operating condition. The final product was tested on the physical appearance, the ability to flow freely through a glass funnel and the mixing property with deionized (DI) water (as discussed in the earlier section). Figure 5a shows the ternary plot indicating the final products obtained for the fifty different ratios. The three axes of the ternary plots correspond to the weight fractions of nanoparticles, total water, and PPG. In order to better interpret the results of ternary plot, the amount of free water was calculated for all the fifty cases based on experimentally-determined relation between total water to PPG ratio and free water to PPG ratio. Figure 5b shows a second ternary plot with free water as one of the axes in place of total water. Several key observations can be deduced from these plots. Depending on the ratio, three different types of products were obtained – encapsulated PPG powder (EPP), mousse and PPG-nanoparticle mixture.

As mentioned earlier, the physical appearance of EPP was dry powder which flows freely through a glass funnel. The range of total water to PPG (TW/PPG) varied from 2 to infinity. The value infinity corresponds to the cases with no PPG (or negligible PPG) such as the ratio of 1:60:0. The case with the maximum PPG/water ratio = 0.5 was 1:4:2 which corresponds to the case with maximum amount of PPG that can be encapsulated for a fixed amount of silica nanoparticles. The range of free water to PPG ratio (FW/PPG) varies from 0 to infinity. (Note that for the case with no PPG particles, total water is equal to free water). It shows that for successful formation of EPP, the presence of mobile, free water is not required. However, in these cases the PPG particles still have thin liquid films (as verified by CLSM) which assist in formation of EPP.

A homogeneous mousse (similar to a shaving cream) was obtained for certain ratios, for instance 1:40:4. It is to be noted that when no PPG particles were present in the system and the ratio of water to nanoparticles was sequentially increased from 1:1 to 80:1, no mousse

formation was obtained for any case. Water-in-air powders were obtained for 1:1 to 60:1 and for higher ratios (70:1, 80:1) two separate phases of nanoparticle and water were obtained. Mousse formation was only observed when there were PPG particles in the system. It shows that presence of PPG influences the formation of mousse. Interestingly, the mousse was only
5 seen when the ratio of water to silica nanoparticle was ≥ 30 . The range of total water to PPG ratio (TW/PPG), where mousse formation was obtained, was 3.75 to 30. The range of free water to PPG ratio (FW/PPG) was 0 to 16.25. Another interesting observation in this case was that transitional inversion from mousse to water-in-air powder was obtained by increasing the amount of PPG in the system while keeping the ratio of nanoparticle to water
10 constant. For example: for the samples with fixed nanoparticles to PPG ratios of 1:2, mousse formation was seen for ratio of water to nanoparticles ≥ 30 , e.g., samples corresponding to 1:30:2 and 1:40:2 ratios. To obtain water-in-air powder, the amount of PPG was needed to be increased which reduced the amount of free water in the system. For example, water-in-air powder was obtained for 1:30:4 and 1:40:8. This transitional inversion from mousse to dry-
15 water seems to be a complex interplay of amount of free water, ratios of NP: water: PPG. Understanding this mechanism of phase inversion is quite complex and deserves further investigations in future.

The physical appearance of this product was dry powder and it looks quite similar to EPP. One of the examples of this case is just the mixture of PPG and nanoparticles with no
20 water or negligible water (Example: Ratio = 1:0:1). The final product in these cases is expected to be dry because of presence of no or minimal water. However, in this case PPG particles are not encapsulated by silica nanoparticles but rather form a homogenous mixture of PPG-nanoparticles. Such product does not flow freely through glass funnel. To further differentiate this product with EPP, a small amount of the sample was mixed with excess
25 deionized water. It resulted in instant swelling of PPG particles as they were not encapsulated. The range of total water to PPG ratio (TW/PPG) for this product was found to be small and between 0.0625-4 which shows that this product was typically formed when amount of PPG is high in the system as can be seen in the ternary plot. Moreover, the amount of free water for all the cases for this product was zero. Figure 5b shows that how all the
30 scattered points corresponding to this PPG-Nanoparticle mixture in ternary plot (left) with total water converge to x-axis corresponding to zero free water.

The encapsulation of particles via water-in-air powder offers a robust technique to encapsulate hydrophilic particles of different sizes ranging from microns to nanometers. In this section, we discuss encapsulation of hydrophilic nanoparticles to demonstrate this

concept. Fluorescently-tagged silica nanoparticles (FL-NP) of diameter 10 nm were used in this case. These nanoparticles show green fluorescence in the presence of UV light. First, 2.5 gm of hydrophobic silica nanoparticles and 25 gm of 0.5 wt% FL-NP solution was taken in a blending cup. This mixture with nanoparticles to FL-NP solution ratio of 1:10 (by weight) was blended at 16,000 rpm for 1 minute. The product resulted in a dry, white powder (Encapsulated FL-NP Powder, EFP) that flows freely through a glass funnel. This EFP was then visualized under UV-light. No green fluorescence was observed indicating complete encapsulation of FL-NP particles. The particle size was calculated to be 27 ± 12 microns by analyzing at least 200 particles. Note that the particle size in this case was smaller than the encapsulated PPG powder case (39 ± 25 microns).

To verify the complete encapsulation of the FL-NP, 0.4 gm of the EFP was mixed with 19.6 gm of deionized water in a blending cup. The sample was vigorously hand shaken for 1 minute and then placed on LabQuake® shaker (Barnstead Thermolyne) at room temperature for agitation for 24 hours. No green fluorescence was observed in the bulk aqueous phase indicating total encapsulation of the FL-NPs. A small amount of sample (1 ml) was taken from the bulk and was analyzed using UV-spectroscopy. No peak corresponding to the FL-NP was observed confirming complete encapsulation of FL-NP. Then, 2.5 gm of ethanol was added to the sample and was mixed vigorously to break the encapsulation. The green fluorescence observed under UV-light indicates release of FL-NP in the bulk solution.

In the aforementioned case, the ratio of hydrophobic silica nanoparticles to FL-NP solution was 1:10 by weight. This ratio was then varied from 1:1 to 1:80 using two different concentration (0.5 wt% and 1 wt%) of FL-NP in the aqueous phase. The results are compared with the case with no FL-NP (deionized water).

Water-in-air powders were obtained for all cases for aqueous phase/silica nanoparticles ratio ≤ 60 , irrespective of the FL-NP concentrations. This shows that the presence of hydrophilic nanoparticles in the aqueous phase does not affect the water-in-air powder formation. For the higher ratios such as 1:70, a small amount of powder was formed which floated on top of the FL-NP solution indicating that only small portion of the aqueous solution was encapsulated. Interestingly, no mousse formation was observed in these cases, in contrast with the PPG encapsulation cases.

The encapsulated PPG particles can be used in conformance control in oil fields. The application includes blocking high permeability channels, fractures, and thief zones in oil reservoirs to prevent channeling of injection fluids. Since, most of these reservoirs are at temperatures higher than 25 °C, it becomes vital to study the effect of high temperature on the

degree of encapsulation. To study this, custom-designed borosilicate glass vessels were built which can be sealed using Teflon-threaded caps. The chemical-resistant O-rings provided a leak-proof system at high temperatures. Then, mixtures of EPP (obtained with a ratio of nanoparticles: water (20 wt% NaCl): PPG (2G-110) = 1: 10: 2) and deionized water (1:49) (in
 5 these vessels) were placed in an oven operating at 80 °C or 125 °C. These samples were periodically centrifuged to measure any release of PPG (2G-110) particles. Even after one month, no PPG particles were released for both the temperatures. This shows that the encapsulation of the micro-particles is robust even at higher temperatures. This makes the proposed encapsulation technique lucrative for several applications in subsurface oil field
 10 applications such as conformance control, delayed acid stimulation etc.

Stimuli-responsive release

In an air-water-particle system, the wettability of the particle governs the stability and curvature of the powder surface. In the present case, highly hydrophobic nanoparticles ($\theta > 90^\circ$) stabilizes the water-in-air powder to encapsulate the hydrophilic particles. Surface-
 15 wettability alteration toward water-wetness ($\theta < 90^\circ$) via external stimuli could weaken the powder and could result in transitional phase inversion from water-in-air powder to air-in-water foam. Such inversion will release the particles allowing them to interact with the external phase. In the present work, we focused on change in pH and addition of surfactant as external stimuli to trigger the release of particles.

20 In the first case, the ratio of hydrophobic silica nanoparticles to aqueous phase was fixed to 1:10 by weight. The aqueous phase with varying pH (2 to 12) or different surfactant concentration, C_{surf} (0.01 wt% to 1 wt %) was blended with nanoparticles at 16,000 rpm for 1 minute. It resulted in formation of water-in-air powder for all the runs irrespective of the pH and the presence of surfactant.

25 In the second case, the ratio of hydrophobic silica nanoparticles to aqueous phase was changed to 1:50 by weight and the experiment was repeated. The final products (images taken 60 minutes after the product formation) are shown in Figure 6c and 6d. For $2 \leq \text{pH} \leq 7$, water-in-air powder was formed which flows freely through a glass funnel. For $\text{pH} \geq 10$, a sticky, mousse-like material was formed which does not flow through a glass funnel.

30 Similarly, for the $C_{\text{surf}} \leq 0.1$ wt%, water-in-air powder was obtained and for $C_{\text{surf}} \geq 0.2$ wt%, mousse-like material was formed. For $C_{\text{surf}} = 1$ wt%, the mousse slowly separates with time, resulting in a bottom aqueous phase as shown in Figure 6d (image taken at $t=60$ minutes). These observations are in line with the literature and shows that a change in pH (close to 12) or presence of surfactant (close to 0.2 wt %) could result in transitional inversion. Since this

effect was only observed for the case of a lower nanoparticles to aqueous phase ratio (1:50) and not at a higher ratio (1:10), it shows that in order to alter the surface-wettability of nanoparticles, a critical amount of aqueous phase (high pH or high surfactant concentration) is required for a fixed amount of nanoparticles.

5 Encapsulated PPG Powder, EPP obtained with a ratio of nanoparticles: water (20 wt% NaCl): PPG (2G-110) = 1: 10: 2 was used in this experiment. This EPP was mixed with water of varying pH in the ratio of 1:49 by weight in 50-ml graduated centrifuge tubes. The pH of the deionized water was changed to 2, 4, 7, 10 and 12 by adjusting the concentration by 0.1M hydrochloric acid (HCl) and 0.1M sodium hydroxide (NaOH). The tubes were capped,
10 placed horizontally on a LabQuake® and were agitated at 25 °C. The samples were periodically centrifuged at 3000 rpm for 2 minutes to measure the amount of precipitated PPG. After centrifugation, the tubes were again mixed vigorously and were placed on the shaker.

 Figure 6 shows the percentage release of PPG (2G-110) particles as a function of
15 time. The reproducibility of the result was within $\pm 4\%$. The percentage release which is the ratio of volume of precipitated, swollen PPG to the volume of fully-swollen PPG (as determined in Table S1) was calculated for different times. It is to be noted that swelling time of the non-encapsulated PPG particles used in the present study was only 3 seconds; hence the delayed swelling is due to delayed breaking of the encapsulation. The time required for
20 10% of the particles to be released (t_{10}) was 0.125, 214.6, 341.7, 355.2, and 420.5 hr corresponding to the pH of 12, 10, 7, 4, and 2. As pH increased, the EPP released the PPG faster.

 Encapsulated PPG Powder, EPP obtained with a ratio of nanoparticles: water (20 wt% NaCl): PPG (2G-110) = 1: 10: 2 was also used here. The EPP was mixed with deionized
25 water with varying Amphoam surfactant concentration in the ratio of 1:49 by weight in 50-ml graduated centrifuge tubes. Samples were agitated at room temperature and periodically centrifuged to measure particle release. Figure 8 shows the percentage release of particles as a function of time (log-scale). For higher surfactant concentrations (e.g., 1 wt%), the release of particles was faster as compared to lower surfactant concentrations (0.01 wt%). The time
30 required for 10% of the particles to be released (t_{10}) decreases sharply with increase in surfactant concentration. The value of t_{10} was 3 min, 5 min, 33 min, 56 min, and 600 min for 1wt%, 0.2 wt%, 0.1 wt%, 0.05 wt%, and 0.01 wt%, respectively.

 The time taken to release 10%, t_{10} of sodium/chloride ions was found to be 16.2 min, 220.5 min, 207.8 min, 219.1 min, 268.2 min corresponding to the pH of 12, 10, 7, 4, and 2.

The release of sodium ions was faster for the case of pH = 12 compared to other pH cases. As compared to PPG release data with varying pH, the release was faster for all these cases. However, in both cases, the release was faster at pH = 12.

5 **Example 9: Superparamagnetic Microparticles**

A similar procedure of making encapsulated PPG in dry water was followed as above. However, in the first step when high salinity water (20 wt% NaCl) and PPG micro-particles (size < 600 micron) were mixed in the ratio of 5:1 by weight, additionally, superparamagnetic nanoparticles (0.26 wt% of dispersion) were added to the mixtures. This dispersed mixture of
10 PPG and magnetic nanoparticles (m-NPs) in saline water was then mixed with hydrophobic silica nanoparticles in ratio of 12:1 and mixed at 4000 rpm.

The “magnetically-active” dry-water system was then mixed with low salinity water (1 wt% NaCl). As observed in the previous case, the mixture was fairly dispersible. No surfactant was added in this case. No phase separation was observed even after several days.

15 This dry-water mixture was then placed in a magnetic-induction coil and an oscillating magnetic field was applied. This result in instant localized heating of the superparamagnetic nanoparticles present inside the dry-water (not in the low salinity water phase). This sudden increase in temperature breaks the encapsulations exposing the un-swelled PPG particles to low salinity water allowing them to swell by several orders of magnitudes. The localized
20 temperature could be increased as high as 100 °C and rate of change of temperature could be precisely controlled by initial m-NPs concentration, voltage applied in magnetic induction, and duration of magnetic oscillation applied. Such, magnetic-stimuli responsive swelling/gelling system makes the current invention more robust to apply in various field scale operations. The magnetically-active dry-water mixture can be injected in the reservoirs
25 and the targeted zones such as high permeability regions and fractures can be plugged by applying magnetic field in those zones.

Examples 10: Microparticles obtained by filtration

In the previous examples, the mixing was performed by using a grinder which is
30 typically used in the literature of dry-water production. The dry-water size can be controlled by changing the rpm of the mixer. Higher rpm results in smaller dry-water particles. In the current invention, we developed an alternate method to produce dry-water. Co-injection of surfactant solution and gas through a porous media results in foam generations. Analogous to this process, we developed a system to produce dry-water in which the required shear is

provided due to flow through a porous media rather than rotational kinetic energy in a mixer. A hollow cylindrical filter (pore size: 140 microns) was taken and it was filled by hydrophobic silica nanoparticles and water. The filter was placed in the in-line filter holder and air was injected through the system at 100 psi injection pressure. This results in vigorous
5 in-situ mixing of gas, water and nanoparticles in the filter, which yielded core/shell particles at the in-line filter outlet. The simplicity of this method makes it quite robust alternative to mixer especially when designing process equipment for upscaling operations. The particle size in this case can be controlled by changing filter of varying pore sizes or by injection pressure of gas.

10 The compositions and methods of the appended claims are not limited in scope by the specific compositions and methods described herein, which are intended as illustrations of a few aspects of the claims and any compositions and methods that are functionally equivalent are intended to fall within the scope of the claims. Various modifications of the compositions and methods in addition to those shown and described herein are intended to fall within the
15 scope of the appended claims. Further, while only certain representative compositions and method steps disclosed herein are specifically described, other combinations of the compositions and method steps also are intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of steps, elements, components, or constituents may be explicitly mentioned herein or less, however, other combinations of
20 steps, elements, components, and constituents are included, even though not explicitly stated. The term “comprising” and variations thereof as used herein is used synonymously with the term “including” and variations thereof and are open, non-limiting terms. Although the terms “comprising” and “including” have been used herein to describe various embodiments, the terms “consisting essentially of” and “consisting of” can be used in place of “comprising”
25 and “including” to provide for more specific embodiments of the invention and are also disclosed. Other than in the examples, or where otherwise noted, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood at the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, to be construed in light of the number of
30 significant digits and ordinary rounding approaches.

CLAIMS

What is claimed is:

1. A plurality of core-shell microparticles, wherein the core comprises a hydrophilic liquid and the shell comprises hydrophobic nanoparticles.
2. The microparticles of claim 1, wherein the microparticles are a collection of free flowing solid particle.
3. The microparticles of claim 1 or claim 2, wherein the microparticles have an angle of repose of no greater than about 45°, no greater than about 40°, no greater than about 35°, no greater than about 30°, no greater than about 25°, no greater than about 20°, no greater than about 15°, or no greater than about 10°.
4. The microparticles of any of claims 1-3, wherein the core-shell microparticles have an aspect ratio of at least about 1.25:1, at least about 1.5:1, at least about 1.75:1, at least about 2.0:1, at least about 2.25:1, or at least about 2.5:1.
5. The microparticles according to any of claim 1-4, wherein the microparticles have an average particle size of about 10,000 μm or less, about 7,500 μm or less, about 5,000 μm or less, about 4,000 μm or less, about 3,000 μm or less, about 2,000 μm or less, about 1,250 μm or less, about 1,000 μm or less, about 750 μm or less, about 500 μm or less, about 400 μm or less, about 300 μm or less, about 200 μm or less, about 100 μm or less, about 75 μm or less, about 50 μm or less, about 25 μm or less, or about 10 μm or less.
6. The microparticles according to any of claim 1-5, wherein the microparticles have an average particle size of about 10-10,000 μm , 10-7,500 μm , 10-5,000 μm , 100-5,000 μm , 500-5,000 μm , 1,000-5,000 μm , 1,000-2,500 μm , 2,500-10,000 μm , 5,000-10,000 μm , 2,500-7,500 μm , 10-1,000 μm , about 10-750 μm , about 10-500 μm , about 10-400 μm , about 10-300 μm , about 10-200 μm , or about 10-100 μm .
7. The microparticles according to any of claims 1-6, wherein the hydrophobic nanoparticles have an average particle size less than about 100 nm, less than about 75 nm, less than about 50 nm, less than about 40 nm, less than about 30 nm, or less than about 20 nm.
8. The microparticles according to any of claims 1-7, wherein the hydrophobic nanoparticles have an average particle size between about 5-100 nm, between about

- 5-75 nm, between about 5-50 nm, between about 5-40 nm, between about 5-30 nm, between about 5-20 nm, between about 10-20 nm, or between about 15-20 nm.
9. The microparticles according to any of claims 1-8, wherein the hydrophobic nanoparticles comprise inorganic particles.
 10. The microparticles according to any of claims 1-9, wherein the hydrophobic nanoparticles comprise metal oxide particles.
 11. The microparticles according to any of claims 1-10, wherein the hydrophobic nanoparticles comprise zirconia, titania, silica, ceria, alumina, iron oxide, vanadia, zinc oxide, antimony oxide, tin oxide, alumina-silica, or a mixture thereof.
 12. The composition according to any of claims 1-11, wherein the hydrophobic nanoparticles comprise a metal oxide having a hydrophobic surface treatment.
 13. The composition according to any of claims 1-12, wherein the hydrophobic nanoparticles comprise a metal oxide having a hydrophobic surface treatment comprising alcohols, amines, carboxylic acids, sulfonic acids, phosphonic acids, silanes, titanates, or a mixture thereof
 14. The composition according to any of claims 1-13, wherein the hydrophobic nanoparticles comprise silica having a surface treatment comprising a silane.
 15. The microparticles according to any of claims 1-14, wherein the microparticles comprise superparamagnetic particles.
 16. The microparticles according to any of claims 1-15, wherein the microparticles comprise superparamagnetic particles in an amount of at least 0.01%, 0.05%, 0.10%, 0.15%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% or 0.50% by weight, relative to the total weight of the core-shell microparticles.
 17. The microparticles according to any of claims 1-16, wherein the microparticles comprise magnetite, maghemite, nickel or cobalt nanoparticles.
 18. The microparticles according to any of claims 1-17, wherein the hydrophilic liquid comprises water.
 19. The microparticles according to any of claims 1-18, wherein the hydrophilic liquid comprises an aqueous mixture comprising acid, base, surfactant, polymers, wetting agents, gelling agents or a mixture thereof.
 20. The microparticles according to any of claims 1-19, wherein the hydrophilic liquid comprises an aqueous acid.
 21. The microparticles according to any of claim 1-20, wherein the hydrophilic liquid comprises organic acid, inorganic acid, or mixtures thereof.

22. The microparticles according to any of claims 1-21, wherein the hydrophilic liquid comprises an organic acid selected from formic acid, acetic acid, oxalic acid, tartaric acid, maleic acid, succinic acid, fumaric acid, citric acid, glyoxylic acid, lactic acid, pyruvic acid, propionic acid, chloroacetic acid, trichloroacetic acid, trifluoroacetic acid, butyric acid, toluenesulfonic acid, methanesulfonic acid, trifluoromethane sulfonic acid, and mixtures thereof.
23. The microparticles according to any of claims 1-21, wherein the hydrophilic liquid comprises an inorganic acid selected from hydrochloric acid, hydrofluoric acid, hydrobromic acid, hydroiodic acid, nitric acid, boric acid, perchloric acid, sulfuric acid, phosphoric acid, and mixtures thereof.
24. The microparticles according to any of claims 1-23, wherein the hydrophilic liquid has a pH of less than about 7, less than about 6, less than about 5, less than about 4, less than about 3, less than about 2, or less than about 1.
25. The microparticles according to any of claims 1-23, wherein the hydrophilic liquid has a pH from about 1-7, about 2-6, about 2-5, or about 3-5
26. The microparticles according to any of claims 1-25, wherein the hydrophilic liquid comprises a gelling agent.
27. The microparticle according to any of claims 1-26, wherein the hydrophilic liquid comprises a gelling agent selected from polyacrylamide, polyacrylic acid-polyacrylamide, curdlan and mixtures thereof.
28. A composition comprising the microparticles according to any of claims 1-27 and a carrier.
29. The composition of claim 28, wherein the carrier comprises a gas, a hydrophobic liquid, or a mixture thereof.
30. The composition of claim 28 or claim 29, further comprising one or more acids, wetting agents, oxidizing agents, microbial organism or reactive monomers.
31. A macroemulsion comprising the microparticles according to any of claims 1-30 dispersed in an oil.
32. A method for preparing the microparticles of any of claims 1-27, comprising the step of combining the hydrophilic liquid and hydrophobic nanoparticles and agitating the mixture.
33. The method according to claim 32, wherein the ratio (w/w) of the hydrophilic liquid to hydrophobic nanoparticles is from about 1:1 to 100:1, about 5:1 to 75:1, about 5:1 to 50:1, about 10:1 to 50:1, or about 10:1 to 25:1.

34. The method according to claim 32 wherein the ratio (w/w) of the hydrophobic nanoparticles to superparamagnetic particles (when present) is from about 10,000:1 to 50:1, about 5,000:1 to 50:1, about 2,500:1 to 50:1, about 1,000:1 to 50:1, about 500:1 to 50:1, about 250:1 about 50:1, or about 100:1 to 50:1.
35. The method according to claims 32-34, wherein the agitating comprises stirring a mixture comprising a hydrophilic liquid and hydrophobic nanoparticles, or passing a mixture comprising a hydrophilic liquid and hydrophobic nanoparticles through a filter under pressure.
36. The method according to any of claims 32-34, wherein the agitating comprises stirring a rate of at least 1000 rpm, at least 2000 rpm, at least 3000 rpm, at least 4000 rpm, at least 5000 rpm, at least 6000 rpm, at least 7000 rpm, at least 8000 rpm, at least 9000 rpm, at least 10,000 rpm, at least 15,000 rpm, at least 20,000 rpm, at least 25,000 rpm, at least 30,000 rpm, at least 35,000 rpm, at least 40,000 rpm, at least 45,000 rpm, or at least 50,000 rpm.
37. The method according to any of claims 32-36, further comprising separating the hydrophilic liquid from the hydrophobic particles.
38. A method for delivering a hydrophilic liquid to a location in a well, comprising:
- a) combining the microparticles of any of claims 1-27, or the composition of any of claims 28-30 with a carrier fluid;
 - b) delivering the microparticles or composition to a location in a well;
 - c) causing the microparticles or the composition to reach a fracture surface;
 - d) causing the microparticles to rupture, thereby releasing the hydrophilic liquid.
39. The method according to claim 38, wherein the hydrophilic liquid is delivered during initial fracturing, refracturing, huff-and-puff periods, and combinations thereof.
40. The method according to claims 38 or 39, wherein the microparticles are ruptured by exposure to pressure, electromagnetic radiation, or surfactant.
41. The method according to claims 38-40, wherein at least about 1 g/ft², at least about 5 g/ft², at least about 10 g/ft², at least about 25 g/ft², at least about 50 g/ft², at least about 75 g/ft², at least about 100 g/ft², at least about 125 g/ft², at least about 150 g/ft², or at least about 200 g/ft² is delivered to the fracture surface.
42. The method according to claims 38-41, wherein about 1-200 g/ft², about 5-200 g/ft², about 10-200 g/ft², about 25-200 g/ft², about 50-200 g/ft², about 50-150 g/ft², about 75-125 g/ft², or about 100 g/ft² is delivered to the fracture surface.
43. A method for preparing resin particles, comprising:

- a) providing an hydrophilic solution comprising a polymerizable monomer;
 - b) combining the hydrophilic solution with hydrophobic nanoparticles under conditions suitable to form microparticles of the hydrophilic solution encapsulated by the nanoparticles;
 - c) polymerizing the polymerizable monomer;
 - d) removing the hydrophobic nanoparticles from the resin particles.
44. The method according to claim 43, wherein the resin particles are monodisperse.
45. The method according to claim 43 or 44, wherein polymerizable monomer comprises at least one ethylenically unsaturated compound.
46. The method according to any of claims 43-45, wherein the polymerizable monomer comprises a vinyl compound, a diene, α,β -monoethylenically unsaturated mono- and dicarboxylic acids, an ester, amide or anhydride thereof, or a mixture thereof.
47. The method according to any of claims 43-46, wherein the hydrophilic solution comprises at least one free-radical initiator.
48. The method according to any of claims 43-47, wherein the hydrophilic solution comprises water.
49. The method according to any of claims 43-48, wherein the polymerization is conducted in a hydrophobic solvent.
50. The method according to any of claims 43-49, wherein the polymerization comprises heating or irradiating the microparticles.

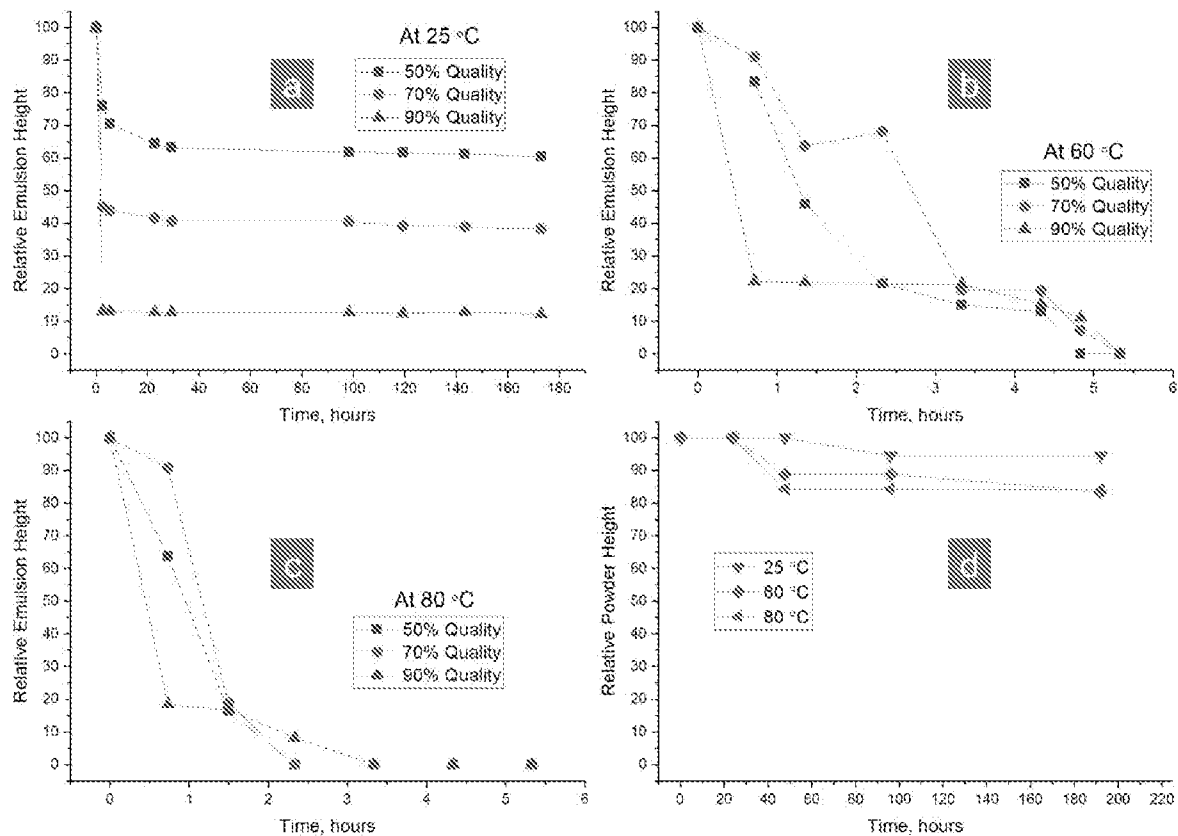


FIG. 1

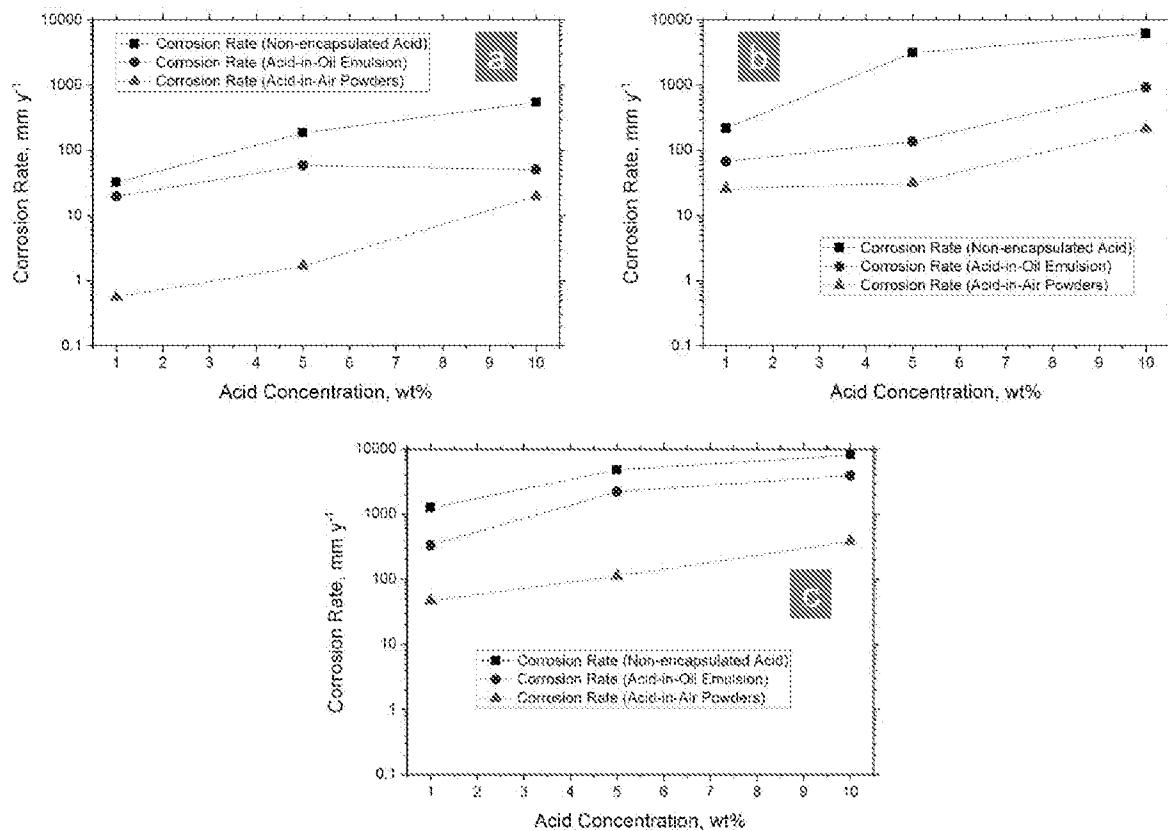


FIG. 2

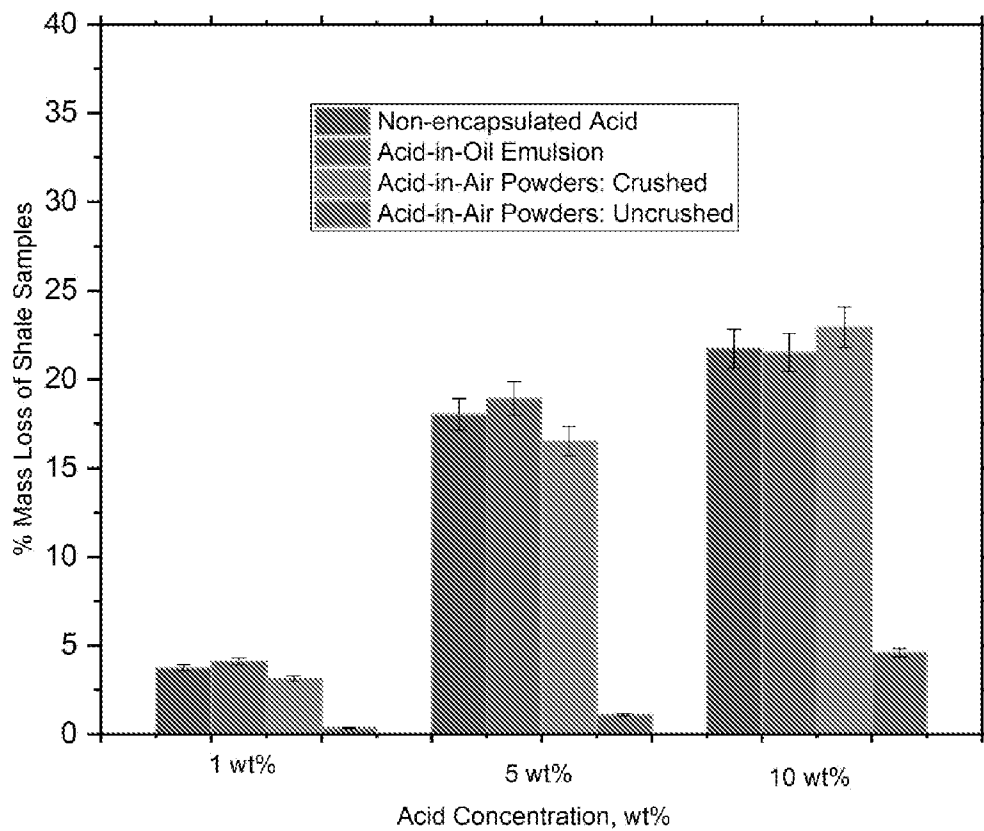


FIG. 3

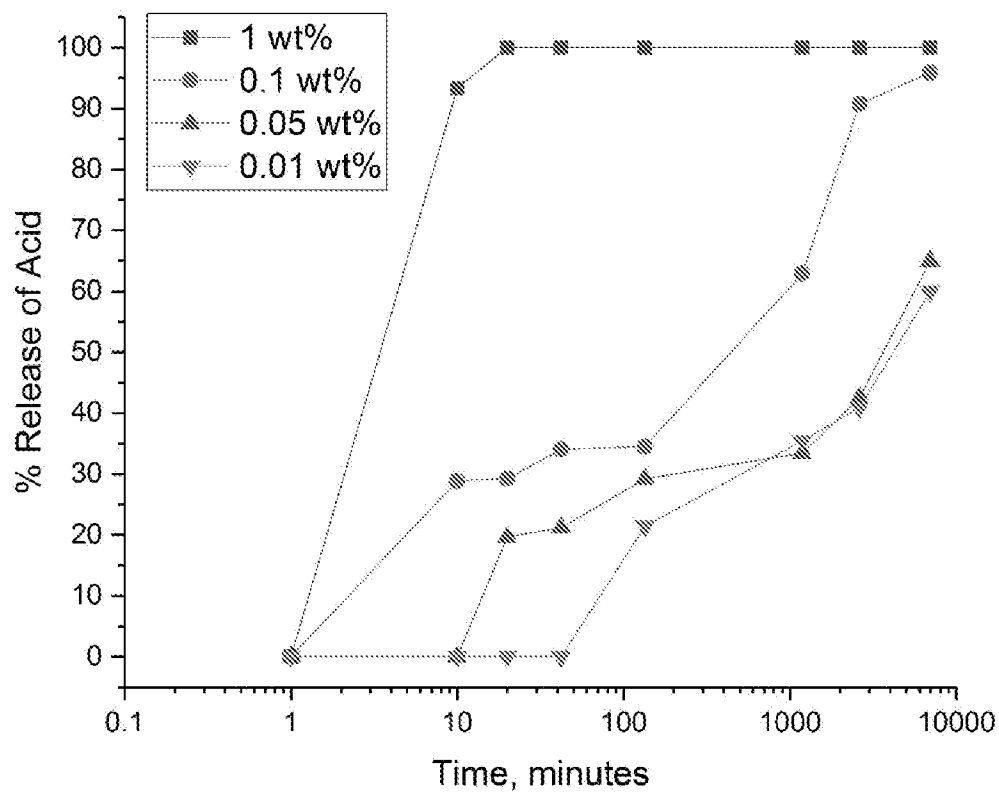


FIG. 4

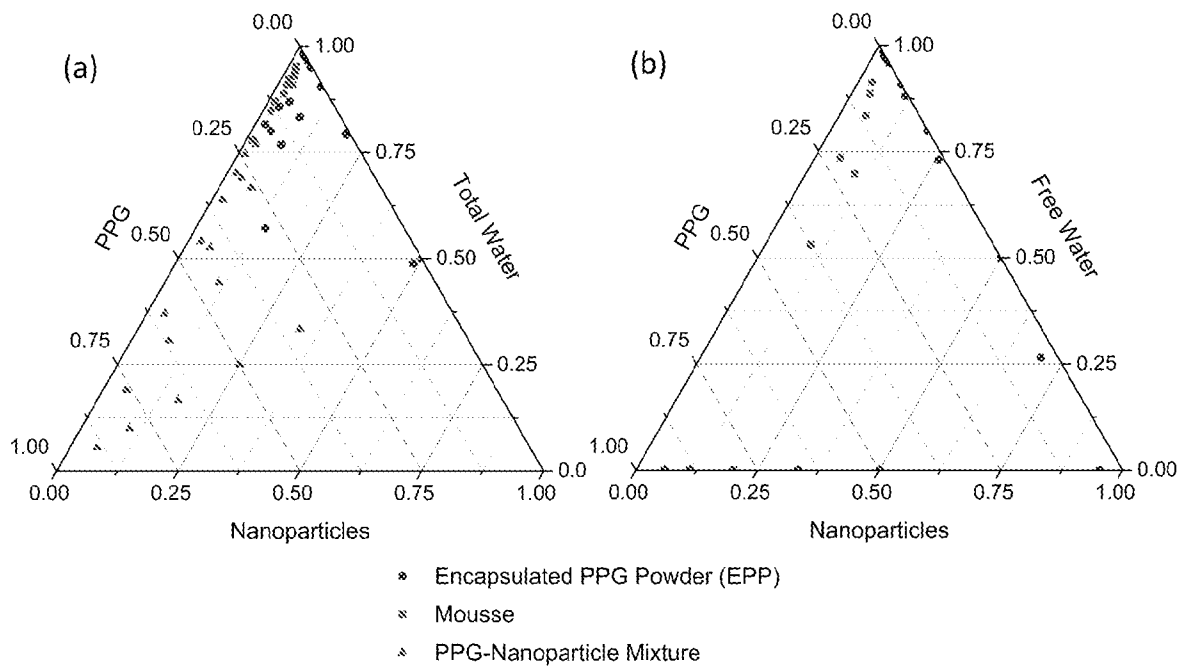


FIG. 5

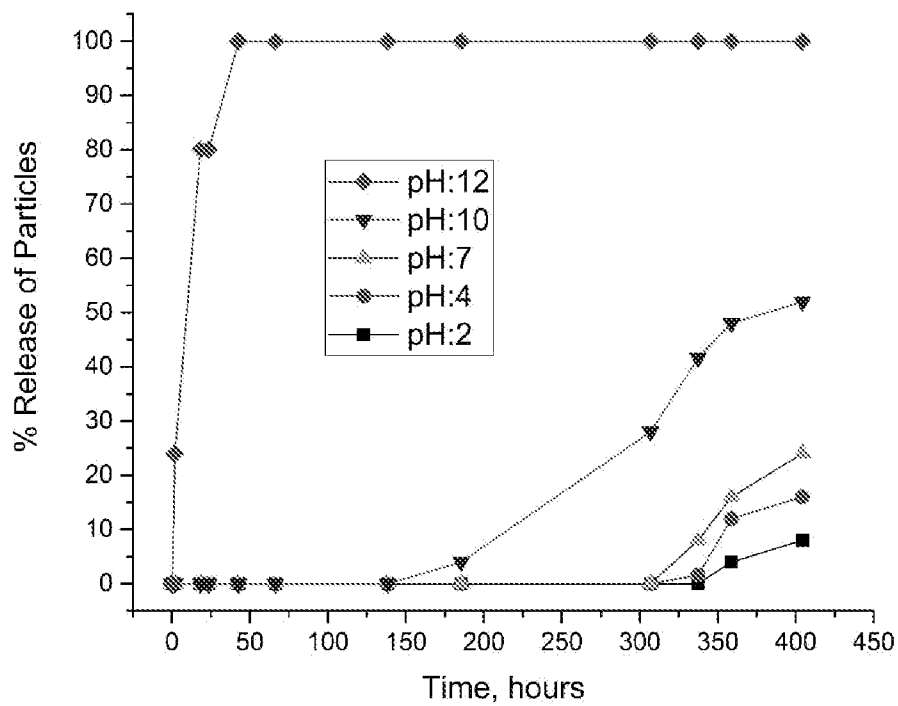


FIG. 6

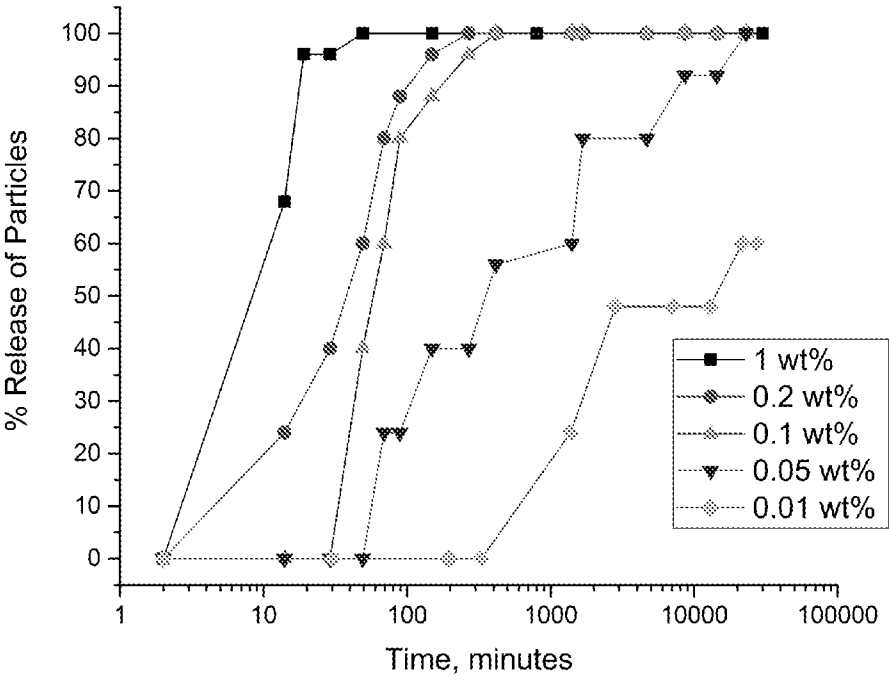


FIG. 7

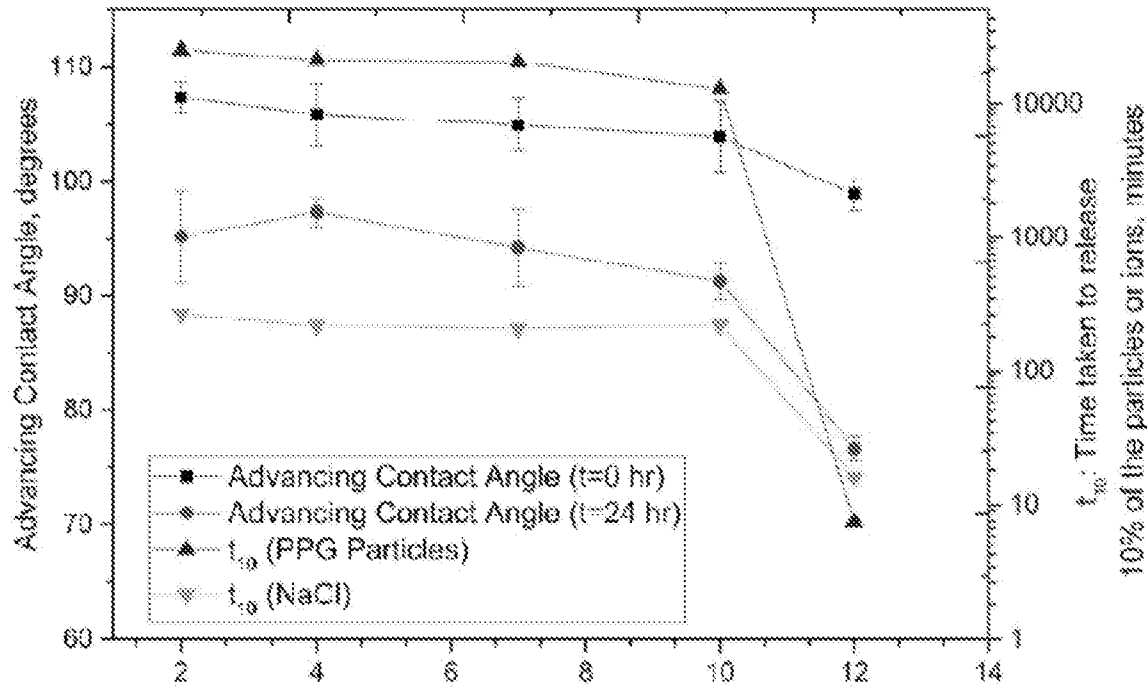


FIG. 8

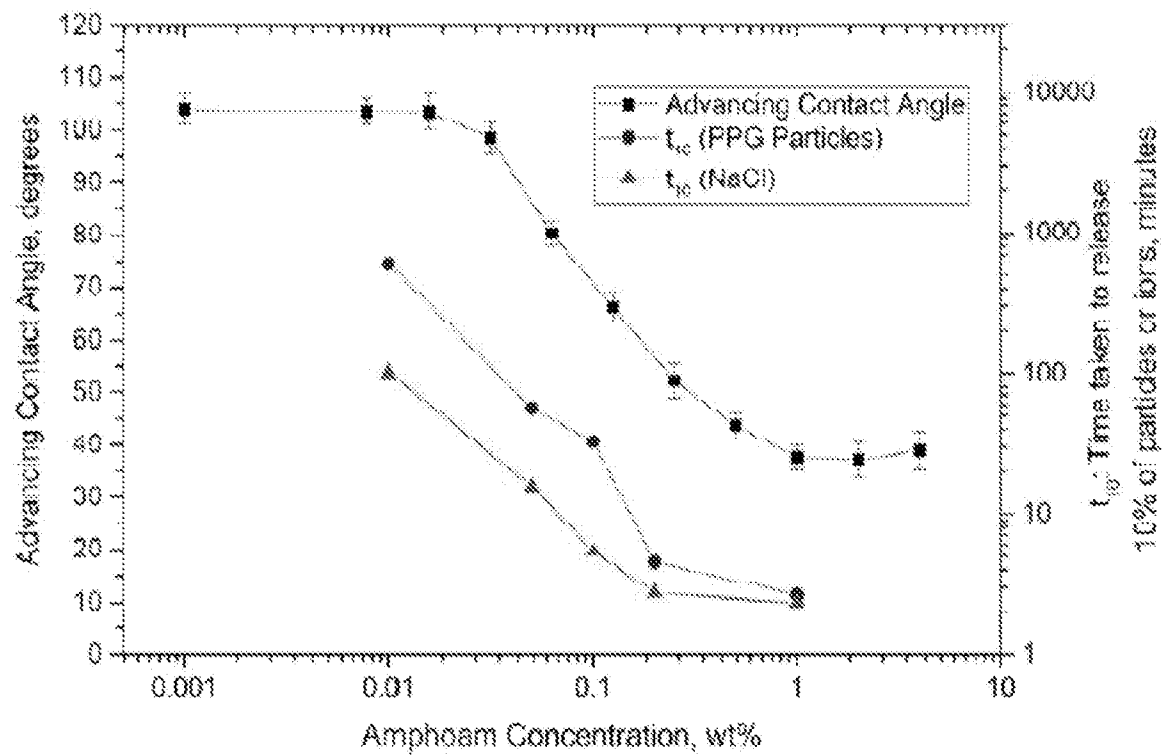


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/43616

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C09K 8/03, 8/72, 8/80, 8/92; E21B 43/27 (2017.01)

CPC - C09K 8/03, 8/032, 8/035, 8/72, 8/725, 8/80, 8/805, 8/92; E21B 43/28

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2014/0187451 A1 (TAMSILIAN, Y et al.) 3 July 2014; abstract; table 1; paragraphs [0001], [0015]-[0017], [0028]-[0029], [0033]-[0035], [0044]; claims 1, 3, 11	1-2, 43 -- 2, 3/1-2, 44, 45/43-44
Y	US 2015/0375429 A1 (MAX-PLANCK-GESELLSCHAFT ZUR FORDERUNG DER WISSENSCHAFTEN E.V.) 31 December 2015; paragraphs [0010], [0064]-[0065], [0071], [0074]	44, 45/44
Y	WO 2015/099735 A1 (HALLIBURTON ENERGY SERVICES, INC.) 2 July 2015; paragraph [0022]	45/43-44
Y	US 2014/0060832 A1 (SOANE ENERGY, LLC) 6 March 2014; paragraphs [0012], [0059]-[0060]	2
Y	US 2010/0069602 A1 (RAICHE, A et al.) 18 March 2010; abstract; paragraphs [0026]-[0027], [0045]	3/1-2
P, X	(EKANEM, EE et al.) Facile microfluidic production of composite polymer core-shell microcapsules and crescent-shaped microparticles. Journal of Colloid and Interface Science. Vol. 498. 15 July 2017. pp. 387-394; entire document	1-2
A	US 2008/0187707 A1 (LI, P et al.) 7 August 2008; entire document	1-2, 3/1-2, 43-44, 45/43-44
A	US 2013/0225458 A1 (QIN, S et al.) 29 August 2013; abstract; entire document, particularly paragraphs [0006], [0019]-[0021], [0030]	43-44, 45/43-44

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

"T"

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

"X"

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

"Y"

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

"&"

document member of the same patent family

Date of the actual completion of the international search

14 September 2017 (14.09.2017)

Date of mailing of the international search report

06 OCT 2017

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

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Shane Thomas

PCT Helpdesk: 571-272-4300

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/43616

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2015/0274538 A1 (DIC CORPORATION) 1 October 2015; entire document	1-2, 3/1-2, 43-44, 45/43-44
A	WO 2009/020594 A1 (AUBURN UNIVERSITY) 12 February 2009; entire document	1-2, 3/1-2, 43-44, 45/43-44

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/43616

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-42, 46-50
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.