

the solid substrate. Contact angle can be measured directly on macroscopic, smooth, nonporous, planar solid substrates by merely placing a droplet of the liquid or solution on the solid substrate and determining the contact angle by any of number of techniques. It is known that majority of natural occurred minerals are water-wet. It is also known that certain hydrocarbon compounds, for example, some conventional quaternary surfactants, amine surfactants and cationic polyacrylamides can be used to reduce the surface energy of certain particulates and make the particulate surface more hydrophobic. However, the "hydrophobicity" imparted by such compounds is not high enough to be included in the term of "extremely high hydrophobicity" as in the case of the present invention. In the present invention, by "extremely hydrophobic" it means that the contact angle of water on the solid substrate is greater than about  $90^{\circ}$ . The chemical compounds that can render the particulate surface extremely hydrophobic are referred as "extremely hydrophobic rendering compounds" (EHRC). EHRC normally are those compounds that contain organosilane or organosiloxane groups or fluoro-organic groups. Because of such groups, EHRC are able to impart hydrophobicity to solid surface to a level that conventional hydrocarbon surfactants or polymers are not able to achieve.

The slurry can be made on the ground or in situ in a subterranean formation. The slurry finds numerous applications in many industries, including

(a) transporting particulates over various distances, either on the surface of the ground, from the surface to a subterranean formation or from a subterranean formation to the surface, and

(b) well service operations including stimulation, drilling, completion, gravel-pack, controlling sand production and the like.

#### DETAILED DESCRIPTION OF THE INVENTION

A gas can be added to the slurry. Suitable gases for use in the slurry include air, carbon dioxide, nitrogen, methane and mixtures thereof. The gas can be introduced into the slurry during preparation thereof. For example, when the slurry is pumped through a pipe at a sufficient rate, gas such as air can be introduced into the slurry. In the present case, by "aqueous liquids" is meant water, salt solutions, water containing an alcohol or other organic solvents, mixtures of water with carbon dioxide and the like. It will be appreciated that the additives other than water in the aqueous liquid are used in amounts or in a manner that does not adversely affect the present invention. The aqueous fluid can also contain polymers which can be linear or cross-linked. For example, in so-called slick-water fracturing, a small amount of polymer is normally added to reduce friction during pumping. The size of particulates in the composition is about 10-100 US mesh, which is about 150 to 1400  $\mu\text{m}$ . It should be understood that the size distribution of particulates can be narrow or wide. Suitable particulates include sand, ceramic, glass beads, bauxite, resin coated sand, carbonates and coal particulates.

There are several approaches to make particulate surfaces extremely hydrophobic. One method is to use certain organosilicon compounds to render the surface of particulates such as sands, ceramic particles, glass spheres and bauxite extremely hydrophobic. The organosilicon compounds include

organosiloxane, organosilane, fluoro-organosiloxane and fluoro-organosilane compounds. The organosiloxane compounds include quaternary siloxane compounds including quaternary polydimethyl siloxane or diquaternary polydimethyl siloxane and siloxane amines. The organosilane compounds include alkylchlorosilane, for example methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, octadecyltrichlorosilane, alkylalkoxysilane compounds, for example methyl-, propyl-, isobutyl- and octyltrialkoxysilanes. The fluoro-organosilane compounds include 2-(n-perfluoro-octyl)-ethyltriethoxysilane, and perfluoro-octyldimethyl chlorosilane. Other types of chemical compounds which can be used to render particulate surface extremely hydrophobic are certain fluoro-substituted compounds, for example certain fluoro-organic compounds. Examples are described in US Patents Nos. 4,564,456; 4,689,085; 5,098,979; 5,209,775; 5,240,760; 5,359,104; 6,132,638 and 6,830,811 and Canadian Patent No. 2,213,168. In some cases, when using the composition described herein, a catalyst might be preferred to speed up the interaction between an EHRC and the particulate surface. For different particulates, certain EHRC may be preferred over others.

There are many types of organosilicon compounds which can be used to impart extreme hydrophobicity to particulate surfaces. One example is an organosilane which can be represented by the formula





wherein R is an organic radical containing 1-50 carbon atoms, X is a halogen, alkoxy, acyloxy or amine containing 1-50 carbon atoms and n has a value of 1 -

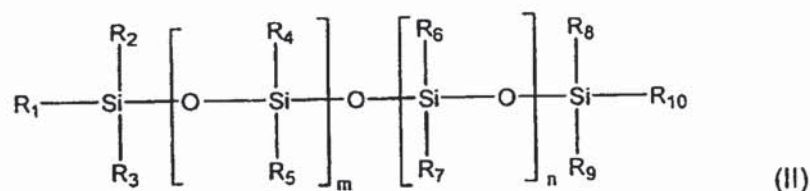
3. Examples of suitable organosilanes include:

CH<sub>3</sub>SiCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>HSiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiCl, CH<sub>3</sub>SiBr<sub>3</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiBr, (CH<sub>3</sub>)<sub>2</sub>SiBr<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiBr<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)SiBr<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiBr,  
 CH<sub>3</sub>HSiBr<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiBr, Si(OCH<sub>3</sub>)<sub>4</sub>, CH<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>,  
 CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>Si[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>,  
 C<sub>6</sub>H<sub>5</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>Si[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (CH<sub>2</sub>=CH<sub>2</sub>)Si(OCH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiOCH<sub>3</sub>, CH<sub>3</sub>HSi(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSi(OCH<sub>3</sub>)<sub>2</sub>,  
 CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>2</sub>=CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>Si(CH<sub>3</sub>COO)<sub>3</sub>, methyl-diethylchlorosilane,  
 butyl-trichlorosilane, diphenyl-dichlorosilane, vinyl-trichlorosilane,  
 methyl-trimethoxysilane, vinyl-triethoxysilane, vinyl-tris(methoxyethoxy)silane,  
 methacryloxypropyl-trimethoxysilane, glycidoxypropyl-trimethoxysilane,  
 aminopropyl-triethoxysilane, divinyl-di-2-methoxysilane, ethyl-tributoxysilane,  
 isobutyl-trimethoxysilane, hexyl-trimethoxysilane, n-octyl-triethoxysilane,  
 dihexyl-dimethoxysilane; trichloro-octadecylsilane and quaternary ammonium

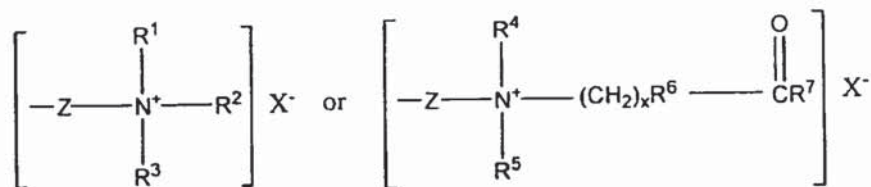


silane including 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride, 3-(trimethylethoxysilylpropyl)didecylmethyl ammonium chloride and triethoxysilyl soyapropyl dimonium chloride.

Different polysiloxane compounds can also be useful for the present invention. Polysiloxanes modified with organic cationic or amphoteric groups including organic betaine polysiloxanes and organic quaternary polysiloxanes are examples. One type of betaine polysiloxane or quaternary polysiloxane is represented by the formula

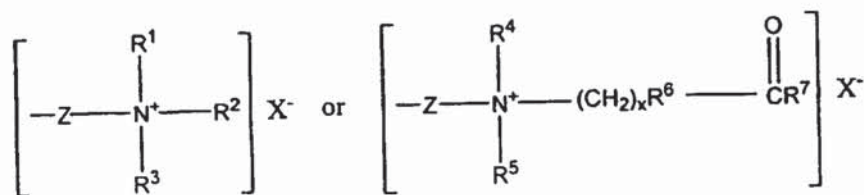


wherein each of the groups  $\text{R}_1$  to  $\text{R}_6$ , and  $\text{R}_8$  to  $\text{R}_{10}$  represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_7$  represents an organic betaine group for betaine polysiloxane, for example betaine polysiloxane copolyol, or an organic quaternary group for quaternary polysiloxane, and may contain a hydroxyl group or other functional groups containing N, P or S, and have different numbers of carbon atoms, and  $m$  and  $n$  are from 1 to 200. For example when  $\text{R}_7$  is an organic quaternary group it can be represented by the group



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wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{Z}$ ,  $\text{X}^-$  and  $x$  are defined above. Such compounds are commercially available from Degussa Corporation or Dow Corning Corporation. It should be apparent to those skilled in the art that there are different mono- and di-quaternary polysiloxanes, mono- and di-betaine polysiloxanes and other organo-modified polysiloxane compounds which can be useful in the present invention. These compounds are widely used in personal care products, for example in US patents 4,054,161; 4,891,166; 5,235,082; 5,306,434; 5,474,835; 5,616,758; 6,277,361 and 6,482,969.

Another example of organosilicon compounds which can be used in the composition of the present invention are fluoro-organosilane or fluoro-organosiloxane compounds in which at least part of the organic radicals in the silane or siloxane compounds are fluorinated. Suitable examples are fluorinated chlorosilanes or fluorinated alkoxysilanes including 2-(n-perfluoro-octyl)ethyltriethoxysilane, perfluoro-octyldimethyl chlorosilane,  $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2$ ,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  and  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ . Other compounds which can be used are fluoro-substituted compounds, for example, certain fluoro-organic compounds.



The slurry according to the present invention can be prepared, for example, by mixing water with the particulates and an EHRC. Normally sufficient shear is needed. Alternatively, the particulates can be first treated by contacting a fluid medium containing an EHRC to cause the particulates to become extremely hydrophobic and then separating the particulates from the medium. The fluid medium can be a liquid or a gas. The hydrophobic particulates can later be used to make slurry. Water is the most preferred aqueous liquid for making the slurry. Certain salts, some conventional hydrocarbon surfactants or polymers can be added to the slurry at concentrations and in a manner which would not adversely affect the slurry. For example, when conventional surfactants, polymers or other additives are added to the slurries, one should try to avoid forming insoluble precipitates with the EHRC, or making large changes to the surface energy of the particulate surface, or greatly reducing the surface tension of the aqueous liquid. In some cases, a very low surface tension of the aqueous liquid is not desirable. When the surface tension of the liquid is too low, more water can be added or some of the aqueous liquid can be replaced with new water.

The slurries can be prepared on surface (above ground) or in a subterranean formation where the particulates, an aqueous fluid, and an EHRC, for example a di-quaternary polysiloxane, are mixed in situ. Examples of situations where in situ mixing is used include drilling and wellbore cleanout operations. Alternatively, the particulates can be first mixed with a liquid in which an EHRC is dispersed or dissolved and then the particulates separated from the

liquid or dried. The thus treated particulates can subsequently be used to make the slurry. Various proppants including sands, ceramic particulates or resin coated sands can be treated according to the present invention during manufacturing process. The thus prepared hydrophobic particulates can be used as proppants in fracturing operations. Depending on the amount and size of the particulates in the slurry, a wide range of EHRC concentration can be used to render the particulate surface extremely hydrophobic. Usually the amount of EHRC added is very small and has no apparent effect on the viscosity of the liquid to which it is added. For example, the concentration of EHRC in the slurry can be as low as a few ppm to hundreds of ppm. In most applications, it is unnecessary to add EHRC in an amount larger than 1 percent of the total liquid.

The following examples serve to illustrate the concepts of the present invention.

#### Example 1

50 ml of water and 50 grams of 20/40 mesh fracturing sands were added into each of two glass bottles (200ml). 0.5 ml of Tegopren 6923, a di-quaternary polysiloxane from Degussa Corp., was added into one of the bottles and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. In the bottle containing Tegopren 6923, the volume of the settled sands was about 40 percent greater than the one without. When the bottles were tilted, the settled sands in the bottle with straight water tended to

move as individual sand grains, while the settled sands containing Tegopren 6923 tended to move as cohesive masses.

#### Example 2

50 ml water, 50 grams of 20/40 mesh fracturing sands, 0.5 ml of Tegopren 6923 and 0.1 ml of Aquard 18-50, a hydrocarbon quaternary ammonium salt from Akzo Nobel Corp., was mixed into a glass bottle (200ml). The bottles were vigorously shaken and then let stand to allow sands settle down. The sand grains immediately following agitation were fully distributed in water making stable slurry. After one hour, about half amount of sands settled down to the bottom while the other half was floating on the top.

#### Example 3

100 ml of water and 50 grams of 20/40 mesh ceramic proppants were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810, a capryl/capramidopropyl betaine from Degussa Corp., and 1 ml of a solution containing 20% Tegopren 6924, a di-quaternary polysiloxane from Degussa Corp., and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow proppants settle down. In the one containing Tegopren 6924 about 25% of proppants was floating on the top and the remaining 75% settled on the bottom. The volume of the 75% settled proppants was still significantly larger than the control one. When the bottles were tilted, the settled proppants in the bottle with straight water tended to move as individual



grains, while the settled proppants containing Tegopren 6924 tended to move as cohesive masses.

#### Example 4

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.1 ml of Tegopren 6924 and 0.1 ml of TEGO Betaine 810, were added and further added 2 wt% KCl. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. In the bottle containing Tegopren 6924, about 15% of sands was floating on the top and the remaining 85% settled on the bottom. The volume of the 85% settled sand was still significantly larger than the control one. When the bottles were tilted, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands containing Tegopren 6924 tended to move as cohesive masses.

#### Example 5

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. After thoroughly mixing the sands were separated from the liquid and dried at room temperature. The pre-hydrophobonized sands were mixed with 100ml water and shaken vigorously. In the bottle containing Tegopren 6924, about 40% of sands was floating on the top and the remaining 60% settled on the bottom. The volume of the 60% settled

sand was still significantly larger than the control one. When the bottles were tilted, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands containing Tegopren 6924 tended to move as cohesive masses.

#### Example 6

100 ml of water and 50 grams of coal particulates were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. The other bottle was used as control. In the bottle containing Tegopren 6924, about 45% of coal particulates was floating on the top and the remaining 55% settled on the bottom. The volume of the 55% settled coal particulates was about 15% smaller than the control one.

#### Example 7

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.03 ml of Maquat QSX, a quaternary silane compound characterized as triethoxysilyl soyapropyl dimonium chloride in butylene glycol, was added into one of the bottles. The other bottle was used as control. After being thoroughly mixed the liquid above the settled sand was discarded and replaced with same amount of water. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. In the bottle containing Maquat QSX, about 5% of sands was floating on the top and remain 95% settled on the bottom. The volume of the 95% settled sand was still significantly larger than the

control one. When the bottles were tilted, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands containing Maquat QSX tended to move as cohesive masses.

#### Example 8

100 ml of water and 50 grams of 20/40 mesh resin coated sands were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow resin coated sands settle down. The volume of settled sands containing Tegopren 6924 is about twice of that in the control one.

As mentioned above, the present invention is particularly useful in many applications in the petroleum industry as well as in other industries. Examples include various well service operations including hydraulic fracturing, gravel pack, wellbore cleanout and drilling, particulate transportation through pipe lines and sand blasting.

When used in a hydraulic fracturing operation, a large amount of proppants can effectively be transported into subterranean formation without using a viscosifier. It is not only cost-effective but also eliminates damage to the formation and proppant pack caused by polymer residues. An EHRC, for example a di-quaternary polysiloxane can be added to a water-based fracturing fluid containing proppants to make the slurry and then pumped into the formation during the proppant stage. Various aqueous fracturing fluids including water,



brine, linear polymer fluid, cross-linked polymer fluid and viscoelastic surfactant fluid can be used. It is particularly beneficial to use the slurry in so-called slick-water fracturing treatment. In conventional slick-water fracturing operations, due to the low viscosity of the fluid, only low concentration of proppants can be effectively pumped deep into a formation, and moreover the proppants tend to settle down on the bottom of the fracture, resulting in lower conductivity. With the composition of the present invention, high concentration of proppants can easily be pumped deep into a formation and the proppants are more evenly distributed in the fracture, leading to improved conductivity of the proppant pack. During the fracturing operation, the EHRC can be added on-the-fly. Optionally, one can use proppants already rendered extremely hydrophobic in the fracturing operation. Another benefit of the slurry of the present invention is that the fluid is readily re-useable after flow back from a well. This has great significance considering there is limited water supply in a number of places.

The present invention also provides a new method for preventing proppant flowback after a fracturing treatment. In field operations, proppants can be pumped into a formation using the composition of the present invention. Various aqueous fracturing fluid, for example water, brine, a linear polymer fluid, a cross-linked polymer fluid or a viscoelastic surfactant fluid can be used. Alternatively, a fluid medium containing an EHRC can be pumped into the formation following the proppant stage to mix with particulates already in the formation. The particulates in the slurry tend to move cohesively in contrast to conventional slurries under the same conditions. It is worth noting that the cohesiveness

among the proppant grains in the present slurry originates from hydrophobic interactions, instead of tackiness as described, for example in US Patent 6,047,772.

The slurry of the present invention is particularly useful in gravel-pack operations where sand slurry is normally pumped into a wellbore to prevent excessive amount of sands from flowing into the wellbore from the formation. The present method is cost effective and the sand pack formed has a high conductivity. Similarly, the slurry can also be used in so-called formation consolidation operations. In such an operation, a fluid containing an EHRC is injected into a formation to increase cohesiveness among sand grains to consolidate the formation and to reduce sand production.

In drilling operations, an EHRC can be added directly to a water-based drilling fluid. It is particularly useful when the EHRC is added to water or brine for use as a drilling fluid. During a drilling operation, the fluid forms slurry in situ with cuttings and transports the cuttings out of the wellbore. A gas such as nitrogen or carbon dioxide can be mixed with the slurry during drilling. Since it is not necessary to use polymers or clays to viscosify the fluid, there is much less formation damage. Moreover, the cuttings can be easily removed on the surface and the fluid becomes readily re-useable. Different formations including sandstone, carbonate, shale and coal seams can be drilled using the slurry of the present invention.

Similarly in wellbore cleanout operations, water or brine containing an EHRC can circulate in the wellbore and form slurry with debris in situ. The debris

is subsequently transported out of the wellbore as slurry. The fluid is readily re-useable after separation from the debris.

For transporting particulates through pipelines slurry can be prepared by mixing the ingredients and then pumping the slurry through the pipeline.



## CLAIMS:

1. An aqueous slurry composition comprising:
  - (a) water;
  - (b) particulates; and
  - (c) a chemical compound for rendering the surface of the particulates extremely hydrophobic.
2. The composition of claim 1, wherein the particulates are selected from the group consisting of sand, resin coated sand, ceramic, carbonate, bauxite, shale and coal particulates.
3. The composition of claim 1, wherein the particulates are subterranean formation particulates.
4. The composition of claim 1, wherein the chemical compound is selected from the group consisting of an organosilane, an organosiloxane, a fluoro-organosilane, a fluorro-organosiloxane and a fluoro-organic compound.
5. The composition of claim 1, wherein the chemical compound is an organosilane having the formula



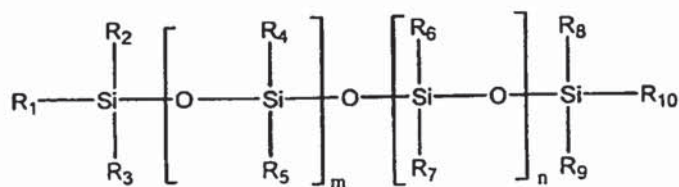
wherein R is an organic radical having 1-50 carbon atoms, X is a halogen, alkoxy, acyloxy or amine and n has a value of 1-3.

6. The composition of claim 5, wherein the organosilane is selected from the group consisting of:
 

CH<sub>3</sub>SiCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>HSiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiCl, CH<sub>3</sub>SiBr<sub>3</sub>,

$(C_6H_5)_3SiBr$ ,  $(CH_3)_2SiBr_2$ ,  $(CH_3CH_2)_2SiBr_2$ ,  $(C_6H_5)_2SiBr_2$ ,  $(CH_3)_3SiBr$ ,  
 $CH_3HSiBr_2$ ,  $(CH_3)_2HSiBr$ ,  $Si(OCH_3)_4$ ,  $CH_3Si(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_3)_3$ ,  
 $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_3Si[O(CH_2)_3CH_3]_3$ ,  $CH_3CH_2Si(OCH_2CH_3)_3$ ,  
 $C_6H_5Si(OCH_3)_3$ ,  $C_6H_5CH_2Si(OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_3)_3$ ,  
 $(CH_3)_2Si(OCH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_2CH_3)_2$ ,  
 $(CH_3)_2Si[O(CH_2)_3CH_3]_2$ ,  $(CH_3CH_2)_2Si(OCH_2CH_3)_2$ ,  $(C_6H_5)_2Si(OCH_3)_2$ ,  
 $(C_6H_5CH_2)_2Si(OCH_3)_2$ ,  $(C_6H_5)_2Si(OCH_2CH_3)_2$ ,  $(CH_2=CH)_2Si(OCH_3)_2$ ,  
 $(CH_2=CHCH_2)_2Si(OCH_3)_2$ ,  $(CH_3)_3SiOCH_3$ ,  $CH_3HSi(OCH_3)_2$ ,  $(CH_3)_2HSi(OCH_3)$ ,  
 $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_2CH_2OCH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(CH_2=CH)_2Si(OCH_2CH_2OCH_3)_2$ ,  $(CH_2=CHCH_2)_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_2CH_2OCH_3)_2$ ,  $CH_3Si(CH_3COO)_3$ , methyltriethoxysilane,  
butyltriethoxysilane, diphenyldichlorosilane, vinyltriethoxysilane,  
methyltrimethoxysilane, vinyltriethoxysilane, vinyltris(methoxyethoxy)silane,  
methacryloxypropyltrimethoxysilane, glycidoxypentyltrimethoxysilane,  
aminopentyltriethoxysilane, divinyl-di-2-methoxysilane, ethyltributoxysilane,  
isobutyltrimethoxysilane, hexyltrimethoxysilane, n-octyltriethoxysilane,  
dihexyldimethoxysilane; trichloro-octadecylsilane, 3-  
(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride, 3-  
(trimethylethoxysilylpropyl)didecylmethyl ammonium chloride and triethoxysilyl  
soyapropyl dimonium chloride.

7. The composition of claim 1, wherein the chemical compound is an organo-siloxane having the formula



wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$ , represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $R_7$  represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and  $m$  and  $n$  are from 1 to 200.

8. The composition of claim 7, wherein the chemical compound is an organic betaine polysiloxane.

9. The composition of claim 8, wherein the chemical compound is an organic betaine polysiloxane, and the values of  $m$  and  $n$  are from 1 to 100.

10. The composition of claim 9, wherein the chemical compound is an organic betaine polysiloxane, wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$  is a methyl group and the values of  $m$  and  $n$  are from 1 to 100.

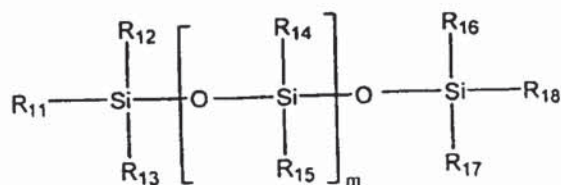
11. The composition of claim 7, wherein the chemical compound is an organic quaternary polysiloxane.

12. The composition of claim 11, wherein the chemical compound is an organic quaternary polysiloxane, and the values of  $m$  and  $n$  are from 1 to 100.

13. The composition of claim 12, wherein the chemical compound is an organic quaternary polysiloxane, and each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$  is a methyl group and the values of  $m$  and  $n$  are from 1 to 100.

14. The composition of claim 1, wherein the chemical compound is an organo-siloxane having the formula





where  $\text{R}_{12}$  to  $\text{R}_{17}$  each represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_{11}$  and  $\text{R}_{18}$  each represents an organic betaine group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and  $m$  is 1 to 200.

15. The composition of claim 14, wherein the chemical compound is a di-betaine polysiloxane.

16. The composition of claim 15, wherein the chemical compound is a di-betaine polysiloxane and the values of  $m$  are from 1 to 100.

17. The composition of claim 16, wherein each of  $\text{R}_{12}$  to  $\text{R}_{17}$  represents a methyl group and the  $m$  is from 1 to 100.

18. The composition of claim 14, wherein the chemical compound is a di-quaternary polysiloxane.

19. The composition of claim 18, wherein the chemical compound is a di-quaternary polysiloxane, and the values of  $m$  are from 1 to 100.

20. The composition of claim 19, wherein each of  $\text{R}_{12}$  to  $\text{R}_{17}$  represents a methyl group and the  $m$  is from 10 to 100.

21. The composition of any one of claims 1 to 20 includes a gas.

22. The composition of claim 21, wherein the gas is selected from the group consisting of air, nitrogen, carbon dioxide, methane and mixtures thereof.

23. A method of producing an aqueous slurry composition comprising the step of mixing water, particulates and a chemical compound for rendering the surface of the particulates extremely hydrophobic.

24. The method of claim 23, wherein the particulates are selected from the group consisting of sand, resin coated sand, ceramic, carbonate, bauxite, shale and coal particulates.

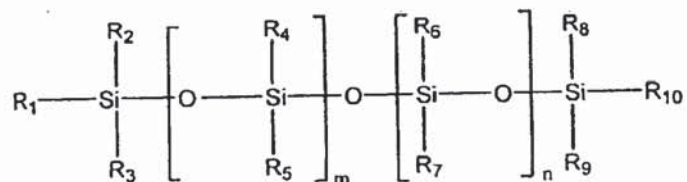
25. The method of claim 23, wherein the chemical compound is selected from the group consisting of an organosilane, an organosiloxane, a fluoro-organosilane, a fluoro-organosiloxane and a fluoro-organic compound.

26. The composition of claim 25, wherein the chemical compound is an organosilane having the formula



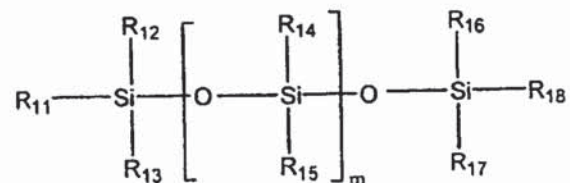
wherein R is an organic radical having 1-50 carbon atoms, X is a halogen, alkoxy, acyloxy or amine and n has a value of 1-3.

27. The composition of claim 25, wherein the chemical compound is an organo-polysiloxane having the formula



wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$ , represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $R_7$  represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and m and n are from 1 to 200.

28. The composition of claim 27, wherein the particulates are sands.
29. The composition of claim 25, wherein the chemical compound is an organo-siloxane having the formula

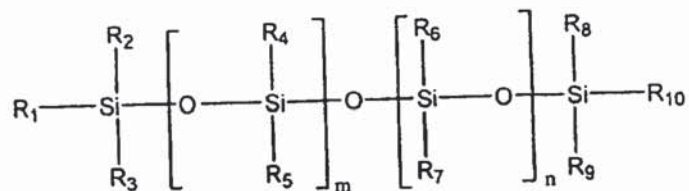


where  $\text{R}_{12}$  to  $\text{R}_{17}$  each represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_{11}$  and  $\text{R}_{18}$  each represents an organic betaine group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and  $m$  is 1 to 200.

30. The composition of claim 29, wherein the particulates are sands.
31. The method of claim 23, including the step of subjecting the slurry composition to shear in the presence of a gas.
32. The method of claim 31, wherein the gas is selected from the group consisting of air, nitrogen, carbon dioxide, methane and mixtures thereof.
33. The method of claim 23, including the steps of contacting the particulate with a medium containing the chemical compound to render the particulate hydrophobic, separating the particulate from the medium; and blending the hydrophobic particulate with water.
34. The method of claim 33, including the step of subjecting the slurry composition to shear in the presence of a gas.
35. The method of claim 33, wherein the gas is selected from the group consisting of air, nitrogen, carbon dioxide, methane and mixtures thereof.



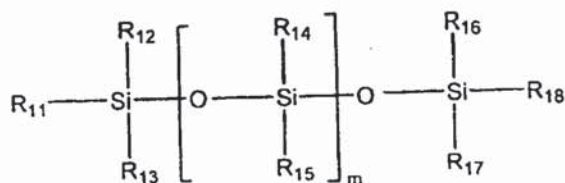
36. The composition of claim 33, wherein the chemical compound is an organo-polysiloxane having the formula



wherein each of R<sub>1</sub> to R<sub>6</sub> and R<sub>8</sub> to R<sub>10</sub>, represents an organic radical containing 1-6 carbon atoms, typically a methyl group, R<sub>7</sub> represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and m and n are from 1 to 200.

37. The composition of claim 36, wherein the particulates are sands.

38. The composition of claim 33, wherein the chemical compound is an organo-siloxane having the formula



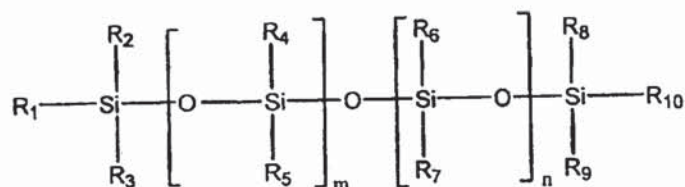
where R<sub>12</sub> to R<sub>17</sub> each represents an organic radical containing 1-6 carbon atoms, typically a methyl group, R<sub>11</sub> and R<sub>18</sub> each represents an organic betaine group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and m is 1 to 200.

39. The composition of claim 38, wherein the particulates are sands.

40. A method of producing an aqueous slurry composition for a well service operation in various formations, comprising the step of mixing water, particulates

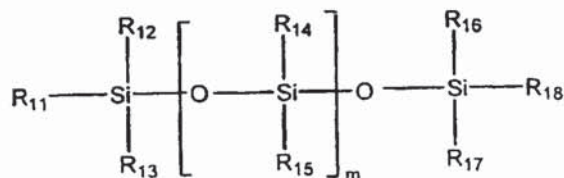
and a chemical compound for rendering the surface of the particulates extremely hydrophobic.

41. The well service operation in claim 40 is selected from the group consisting of hydraulic fracturing, drilling, completion and sand pack operation.
42. The method of claim 40, including the step of subjecting the slurry composition to shear in the presence of a gas.
43. The fluid in Claim 40 can be re-used after separated from the particulates.
44. The composition of claim 40, wherein the chemical compound is an organo-polysiloxane having the formula



wherein each of R<sub>1</sub> to R<sub>6</sub> and R<sub>8</sub> to R<sub>10</sub>, represents an organic radical containing 1-6 carbon atoms, typically a methyl group, R<sub>7</sub> represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and m and n are from 1 to 200.

45. The composition of claim 40, wherein the chemical compound is an organo-siloxane having the formula



where R<sub>12</sub> to R<sub>17</sub> each represents an organic radical containing 1-6 carbon atoms, typically a methyl group, R<sub>11</sub> and R<sub>18</sub> each represents an organic betaine

group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and m is 1 to 200.

46. A method of producing an aqueous slurry composition for transporting particulates through a pipeline, comprising the step of mixing water, particulates and a chemical compound for rendering the surface of the particulates extremely hydrophobic, and pumping the slurry through the pipeline.

47. The composition of claim 46, wherein the particulates are sands.

48. The composition of claim 46, wherein the particulates are coal particulates.



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(54) Title: METHOD FOR MAKING TRANSPORTABLE AQUEOUS SLURRIES BY PARTICULATE HYDROPHOBICIZATION

(57) Abstract: An aqueous slurry composition for use in industries such as the petroleum and pipeline industries includes a particulate, an aqueous liquid and a chemical compound that renders the particulate surface extremely hydrophobic. The slurry is produced by rendering the surface of the particulate extremely hydrophobic during or before making the slurry.

Preferred Proppants, LLC, Preferred Pipeline, LLC, Preferred Resin Sales, LLC, Preferred Resin of Genoa, LLC, Preferred Sands of Wisconsin, LLC, Ex. 1003, p. 446 of 1051

WO 2006/116868 A1

## BACKGROUND OF THE INVENTION

### Field of the Invention

This invention relates to an aqueous slurry composition and to a method of making such a composition.

### Discussion of the Prior Art

Aqueous particulate slurries are commonly used or encountered in many industries including the petroleum, pipeline, construction and cleaning industries. Slurries are mixtures normally consisting of particulates and an aqueous liquid and play an essential role in many industrial operations. For example, slurries are used when transporting particulates above ground, from the surface to a subterranean formation or from a subterranean formation to the surface. The most commonly used particulates include sand, ceramic particles, carbonate particles, glass spheres, bauxite (aluminum oxide), resin coated particulates and coal particulates. The particulate sizes normally range from about 10 to about 100 US mesh, and the particles have densities significantly higher than the density of water. For example, the density of sand is at about  $2.6 \text{ g/cm}^3$  while the density of water is  $1 \text{ g/cm}^3$ . Sand is by far the most commonly used particulate.

To make relatively stable slurry, particulates must be suspended in a liquid medium for a lengthy period at static or/and dynamic conditions. Convention wisdom tells us that the viscosity or viscoelasticity of the liquid medium must be sufficiently high to be able to suspend particulates. The most commonly used method for increasing viscosity or viscoelasticity of a liquid medium is by adding



a viscosifier, for example, a natural or synthetic polymer or a viscoelastic surfactant to the liquid medium. It is not unusual that a polymer is used with a foaming agent in order to take advantage of both viscoelastic and foaming properties. However, the use of polymers in slurries increases cost and results in operational difficulties. In particular applications, for example, hydraulic fracturing of subterranean formations, the use of polymers in slurry impedes oil and gas production due to large amounts of residue left in the formation. As for viscoelastic surfactants, although they have fewer residues compared to normal polymers, their cost is usually much higher. In many other applications such as gravel-pack, well completion and sand transportation through pipelines, it is highly desirable to make stable particulate slurry without using a viscosifier.

Hydraulic fracturing operations are used extensively in the petroleum industry to enhance oil and gas production. In hydraulic fracturing, a fracturing fluid is injected through a wellbore into a subterranean formation at a pressure sufficient to initiate fracturing, which increases oil and gas production. Frequently, particulates, called proppants, are suspended in a fracturing fluid and transported into a fracture as slurry. Proppants include sands, ceramic particulates, glass spheres, bauxite particulates, resin coated sands and other particulates known in the industry. Among them sand is by far the most commonly used proppant. Fracturing fluids in common use include water-based as well as hydrocarbon-based fluids. In water-based fracturing fluids, a polymer or viscoelastic surfactant is normally employed to increase the viscoelasticity of the fluid. In most case the viscoelastic property of the fluids is essential for transporting proppants deep into



a formation. At the last stage of the fracturing treatment, fracturing fluid flows back to the surface and the proppants are left in the fracture forming a proppant pack to prevent the fracture from closing after pressure is released. A proppant-filled fracture provides a highly conductive channel that allows oil and/or gas to seep through more efficiently to the wellbore. The conductivity of the proppant pack plays a dominant role in production enhancement. Polymer residues from fracturing fluids are known to greatly reduce the conductivity of the proppant pack. Compared to polymeric viscosifiers, viscoelastic surfactants cause less damage to formations and proppant packs. However, they are much more expensive. Accordingly, a need exists for a composition for efficiently transporting proppants deep into a formation at low cost while at the same time causing little damage to the formation and proppant pack. Grain size, concentration, and the packing pattern of proppants are also important factors in determining the conductivity. Despite extensive research in recent years, limited progress has been achieved to maximize the conductivity of a proppant pack in a fracture. Therefore, a need exists for making a composition for use in a proppant pack with improved conductivity.

Proppant flowback after fracturing treatments has long been plaguing the petroleum industry. Flowback reduces the amount of proppants in the formation leading to a less conductive fracture. As disclosed, for example in US Patent 6,047,772, various methods have been tried to solve the flowback problem. In one method, resins are used to coat the proppant and make them very tacky. In doing so, the proppant grains tend to agglomerate reducing flowback. This

method is not only expensive, but the tacky resins introduced in the proppant pack tend to reduce its conductivity. Therefore, there is a need for a composition and method for making slurry, which can form a stable proppant pack, which resists proppant flowback while at the same time has a high conductivity.

When drilling subterranean formations for oil and gas, aqueous-based drilling fluids are normally used. During drilling large amounts of particles, called cuttings are generated. Cuttings have different sizes ranging from fines to pebbles. The drilling fluid is circulated through the wellbore to make slurry with the cuttings in situ and transports them out of wellbore. In most cases, polymers as well as clays are added to the drilling fluids to increase their viscosity/viscoelasticity in order to transport the cuttings efficiently. However, polymers as well as clay fines, can easily penetrate pores or thin fractures in a formation and reduce formation permeability significantly, especially near a wellbore. Reduced formation permeability impedes oil and/or gas production. Therefore it is highly desirable to provide a drilling fluid that can make stable slurry in situ with the cuttings and transport them out of the wellbore, while causing little formation damage.

The escalating price of oil and its alarming depletion rate have caused people to consider using coal as an oil substitute. Several factors have slowed the substitution of coal for oil. One factor is the difficulty in transporting coal cost-effectively over long distance through pipelines. It is therefore highly desirable to provide a composition for making coal slurry which is stable, highly fluid and cost-effective to transport.



In oil sand operation massive amount of sands are left after oil is stripped from the sand surface. Finding a more cost effective way to transport sands efficiently over distance through pipelines has long been required in the industry. Thus, a composition and a method for making stable and highly fluid sand slurries at low cost would be quite useful.

The object of the present invention is to meet the above defined needs by providing an aqueous slurry composition, which can be used in a stable, highly conductive proppant pack, for efficiently transporting proppants into a subterranean formation, and for use in transporting cuttings, coal and sand.

#### SUMMARY OF THE INVENTION

Accordingly, the invention relates to an aqueous slurry composition comprising particulates, an aqueous liquid and a chemical compound that renders the surface of the particulates extremely hydrophobic.

The invention also relates to a method of producing an aqueous slurry composition comprising the steps of mixing particulates with an aqueous liquid, and rendering the particulate surface extremely hydrophobic during or before mixing the particulates with the aqueous liquid.

The present invention is based on the discovery that when the surface of the particulates becomes extremely hydrophobic, the slurry has several novel properties. For example, particulates tend to move cohesively instead as individual grains; the bulk volume of settled particulates tend to be significantly greater than in a slurry formed by convention methods under the same conditions; the particulate pack formed tends to have high conductivity and be



easily dewatered, and the slurry tends to be fluid and stable without using a viscosifier. The larger bulk volume of the particulate pack indicates a larger porosity and therefore higher conductivity. This is particularly beneficial for improving fracturing treatment, since, as mentioned above, the conductivity of the proppant pack is the dominant property affecting fracturing treatment. The extremely hydrophobic surface of the particulate further reduces the dragging force exerted by the fluid and makes it more difficult for proppants to be carried away by the fluid. This is particularly beneficial for minimizing proppant flowback after fracturing treatments, leading to increased proppant conductivity. In conventional slurry, viscosity or viscoelasticity of the liquid plays the dominant role while the interfacial interactions between the particulate surface and the liquid play negligible role. However it is discovered in the present invention that when the surface of the particulate becomes extremely hydrophobic, the interfacial interactions between the surface and the aqueous liquid become increasingly important, and even can play a dominant role.

In general, the interfacial interactions between a solid substrate and a liquid mainly depend on the surface properties and the surface tension of the liquid. Normally the macroscopic properties of a surface can be characterized by observing the shape of a liquid droplet on the solid substrate, which is the result of free energy of the surface, as well as the free energy of the liquid. When a liquid does not completely wet a surface, it forms an angle  $\theta$ , which is known as the contact angle. The contact angle is the angle formed between a solid substrate and the tangent line at the point of contact between a liquid droplet and

the solid substrate. Contact angle can be measured directly on macroscopic, smooth, nonporous, planar solid substrates by merely placing a droplet of the liquid or solution on the solid substrate and determining the contact angle by any of number of techniques. It is known that majority of natural occurred minerals are water-wet. It is also known that certain hydrocarbon compounds, for example, some conventional quaternary surfactants, amine surfactants and cationic polyacrylamides can be used to reduce the surface energy of certain particulates and make the particulate surface more hydrophobic. However, the "hydrophobicity" imparted by such compounds is not high enough to be included in the term of "extremely high hydrophobicity" as in the case of the present invention. In the present invention, by "extremely hydrophobic" it means that the contact angle of water on the solid substrate is greater than about  $90^\circ$ . The chemical compounds that can render the particulate surface extremely hydrophobic are referred as "extremely hydrophobic rendering compounds" (EHRC). EHRC normally are those compounds that contain organosilane or organosiloxane groups or fluoro-organic groups. Because of such groups, EHRC are able to impart hydrophobicity to solid surface to a level that conventional hydrocarbon surfactants or polymers are not able to achieve.

The slurry can be made on the ground or in situ in a subterranean formation. The slurry finds numerous applications in many industries, including

(a) transporting particulates over various distances, either on the surface of the ground, from the surface to a subterranean formation or from a subterranean formation to the surface, and



(b) well service operations including stimulation, drilling, completion, gravel-pack, controlling sand production and the like.

#### DETAILED DESCRIPTION OF THE INVENTION

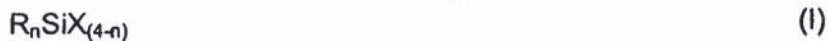
A gas can be added to the slurry. Suitable gases for use in the slurry include air, carbon dioxide, nitrogen, methane and mixtures thereof. The gas can be introduced into the slurry during preparation thereof. For example, when the slurry is pumped through a pipe at a sufficient rate, gas such as air can be introduced into the slurry. In the present case, by "aqueous liquids" is meant water, salt solutions, water containing an alcohol or other organic solvents, mixtures of water with carbon dioxide and the like. It will be appreciated that the additives other than water in the aqueous liquid are used in amounts or in a manner that does not adversely affect the present invention. The aqueous fluid can also contain polymers which can be linear or cross-linked. For example, in so-called slick-water fracturing, a small amount of polymer is normally added to reduce friction during pumping. The size of particulates in the composition is about 10-100 US mesh, which is about 150 to 1400  $\mu\text{m}$ . It should be understood that the size distribution of particulates can be narrow or wide. Suitable particulates include sand, ceramic, glass beads, bauxite, resin coated sand, carbonates and coal particulates.

There are several approaches to make particulate surfaces extremely hydrophobic. One method is to use certain organosilicon compounds to render the surface of particulates such as sands, ceramic particles, glass spheres and bauxite extremely hydrophobic. The organosilicon compounds include



organosiloxane, organosilane, fluoro-organosiloxane and fluoro-organosilane compounds. The organosiloxane compounds include quaternary siloxane compounds including quaternary polydimethyl siloxane or diquaternary polydimethyl siloxane and siloxane amines. The organosilane compounds include alkylchlorosilane, for example methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, octadecyltrichlorosilane, alkyl-alkoxysilane compounds, for example methyl-, propyl-, isobutyl- and octyltrialkoxysilanes. The fluoro-organosilane compounds include 2-(n-perfluoro-octyl)-ethyltriethoxysilane, and perfluoro-octyldimethyl chlorosilane. Other types of chemical compounds which can be used to render particulate surface extremely hydrophobic are certain fluoro-substituted compounds, for example certain fluoro-organic compounds. Examples are described in US Patents Nos. 4,564,456; 4,689,085; 5,098,979; 5,209,775; 5,240,760; 5,359,104; 6,132,638 and 6,830,811 and Canadian Patent No. 2,213,168. In some cases, when using the composition described herein, a catalyst might be preferred to speed up the interaction between an EHRC and the particulate surface. For different particulates, certain EHRC may be preferred over others.

There are many types of organosilicon compounds which can be used to impart extreme hydrophobicity to particulate surfaces. One example is an organosilane which can be represented by the formula



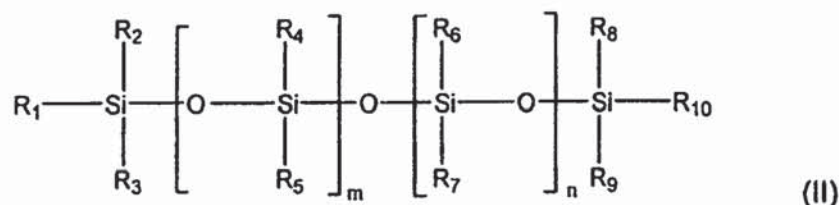
wherein R is an organic radical containing 1-50 carbon atoms, X is a halogen, alkoxy, acyloxy or amine containing 1-50 carbon atoms and n has a value of 1 -

3. Examples of suitable organosilanes include:

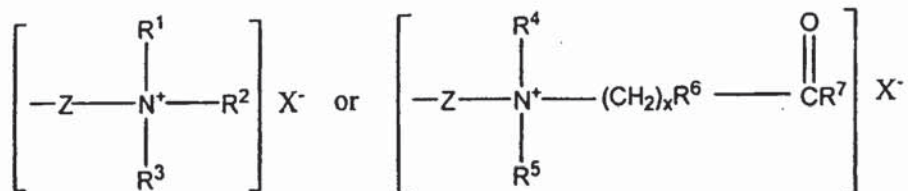
CH<sub>3</sub>SiCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>HSiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiCl, CH<sub>3</sub>SiBr<sub>3</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiBr, (CH<sub>3</sub>)<sub>2</sub>SiBr<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiBr<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)SiBr<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiBr,  
 CH<sub>3</sub>HSiBr<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiBr, Si(OCH<sub>3</sub>)<sub>4</sub>, CH<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>,  
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 (CH<sub>2</sub>=CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>Si(CH<sub>3</sub>COO)<sub>3</sub>, methyltriethylchlorosilane,  
 butyltrichlorosilane diphenyldichlorosilane, vinyltrichlorosilane,  
 methyltrimethoxysilane, vinyltriethoxysilane, vinyltris(methoxyethoxy)silane,  
 methacryloxypropyltrimethoxysilane, glycidoxypyltrimethoxysilane,  
 aminopropyltriethoxysilane, divinyl-di-2-methoxysilane, ethyltributoxysilane,  
 isobutyltrimethoxysilane, hexyltrimethoxysilane, n-octyltriethoxysilane,  
 dihexyldimethoxysilane; trichloro-octadecylsilane and quaternary ammonium

silane including 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride, 3-(trimethylethoxysilylpropyl)didecylmethyl ammonium chloride and triethoxysilyl soyapropyl dimonium chloride.

Different polysiloxane compounds can also be useful for the present invention. Polysiloxanes modified with organic cationic or amphoteric groups including organic betaine polysiloxanes and organic quaternary polysiloxanes are examples. One type of betaine polysiloxane or quaternary polysiloxane is represented by the formula



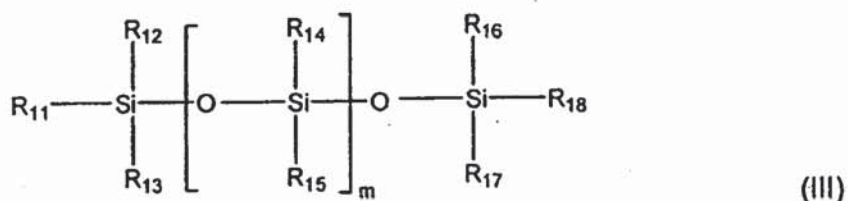
wherein each of the groups  $\text{R}_1$  to  $\text{R}_6$ , and  $\text{R}_8$  to  $\text{R}_{10}$  represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_7$  represents an organic betaine group for betaine polysiloxane, for example betaine polysiloxane copolyol, or an organic quaternary group for quaternary polysiloxane, and may contain a hydroxyl group or other functional groups containing N, P or S, and have different numbers of carbon atoms, and  $m$  and  $n$  are from 1 to 200. For example when  $\text{R}_7$  is an organic quaternary group it can be represented by the group



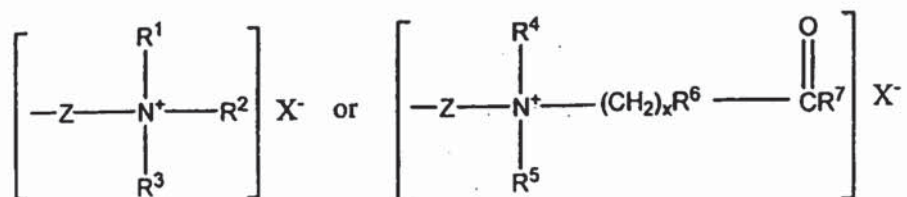


wherein  $R^1, R^2, R^3$  are alkyl groups with 1 to 22 carbon atoms or alkenyl groups with 2 to 22 carbon atoms.  $R^4, R^5, R^6$  are alkyl groups with 1 to 22 carbon atoms or alkenyl groups with 2 to 22 carbon atoms;  $R^6$  is  $-O-$  or the  $NR^8$  group,  $R^8$  being an alkyl or hydroxyalkyl group with 1 to 4 carbon atoms or a hydrogen group; Z is a bivalent hydrocarbon group with at least 4 carbon atoms, which may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group; x is 2 to 4; The  $R^1, R^2, R^3, R^4, R^5, R^6$  may be the same or the different, and  $X^-$  is an inorganic or organic anion. Such compounds are commercial available from Degussa Corporation and Dow Corning Corporation.

Other example of organo-modified polysiloxanes include di-betaine polysiloxanes and di-quaternary polysiloxanes, which can be represented by the formula



wherein the groups  $R_{12}$  to  $R_{17}$  each represents an organic radical containing 1-6 carbon atoms, typically a methyl group, both  $R_{11}$  and  $R_{18}$  group represent an organic betaine group for di-betaine polysiloxanes or an organic quaternary group for di-quaternary, for example Quaternium 80 (INCI), and may contain a hydroxyl group or other functional groups containing N, P or S, and have different numbers of carbon atoms, and m is from 1 to 200. For example when  $R_{11}$  and  $R_{18}$  is an organic quaternary group it can be represented by the group



wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{Z}$ ,  $\text{X}^-$  and  $x$  are defined above. Such compounds are commercially available from Degussa Corporation or Dow Corning Corporation. It should be apparent to those skilled in the art that there are different mono- and di-quaternary polysiloxanes, mono- and di-betaine polysiloxanes and other organo-modified polysiloxane compounds which can be useful in the present invention. These compounds are widely used in personal care products, for example in US patents 4,054,161; 4,891,166; 5,235,082; 5,306,434; 5,474,835; 5,616,758; 6,277,361 and 6,482,969.

Another example of organosilicon compounds which can be used in the composition of the present invention are fluoro-organosilane or fluoro-organosiloxane compounds in which at least part of the organic radicals in the silane or siloxane compounds are fluorinated. Suitable examples are fluorinated chlorosilanes or fluorinated alkoxysilanes including 2-(n-perfluoro-octyl)ethyltriethoxysilane, perfluoro-octyldimethyl chlorosilane,  $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2$ ,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  and  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ . Other compounds which can be used are fluoro-substituted compounds, for example, certain fluoro-organic compounds.

The slurry according to the present invention can be prepared, for example, by mixing water with the particulates and an EHRC. Normally sufficient shear is needed. Alternatively, the particulates can be first treated by contacting a fluid medium containing an EHRC to cause the particulates to become extremely hydrophobic and then separating the particulates from the medium. The fluid medium can be a liquid or a gas. The hydrophobic particulates can later be used to make slurry. Water is the most preferred aqueous liquid for making the slurry. Certain salts, some conventional hydrocarbon surfactants or polymers can be added to the slurry at concentrations and in a manner which would not adversely affect the slurry. For example, when conventional surfactants, polymers or other additives are added to the slurries, one should try to avoid forming insoluble precipitates with the EHRC, or making large changes to the surface energy of the particulate surface, or greatly reducing the surface tension of the aqueous liquid. In some cases, a very low surface tension of the aqueous liquid is not desirable. When the surface tension of the liquid is too low, more water can be added or some of the aqueous liquid can be replaced with new water.

The slurries can be prepared on surface (above ground) or in a subterranean formation where the particulates, an aqueous fluid, and an EHRC, for example a di-quaternary polysiloxane, are mixed in situ. Examples of situations where in situ mixing is used include drilling and wellbore cleanout operations. Alternatively, the particulates can be first mixed with a liquid in which an EHRC is dispersed or dissolved and then the particulates separated from the



liquid or dried. The thus treated particulates can subsequently be used to make the slurry. Various proppants including sands, ceramic particulates or resin coated sands can be treated according to the present invention during manufacturing process. The thus prepared hydrophobic particulates can be used as proppants in fracturing operations. Depending on the amount and size of the particulates in the slurry, a wide range of EHRC concentration can be used to render the particulate surface extremely hydrophobic. Usually the amount of EHRC added is very small and has no apparent effect on the viscosity of the liquid to which it is added. For example, the concentration of EHRC in the slurry can be as low as a few ppm to hundreds of ppm. In most applications, it is unnecessary to add EHRC in an amount larger than 1 percent of the total liquid.

The following examples serve to illustrate the concepts of the present invention.

#### Example 1

50 ml of water and 50 grams of 20/40 mesh fracturing sands were added into each of two glass bottles (200ml). 0.5 ml of Tegopren 6923, a di-quaternary polysiloxane from Degussa Corp., was added into one of the bottles and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. In the bottle containing Tegopren 6923, the volume of the settled sands was about 40 percent greater than the one without. When the bottles were tilted, the settled sands in the bottle with straight water tended to

move as individual sand grains, while the settled sands containing Tegopren 6923 tended to move as cohesive masses.

#### Example 2

50 ml water, 50 grams of 20/40 mesh fracturing sands, 0.5 ml of Tegopren 6923 and 0.1 ml of Aquard 18-50, a hydrocarbon quaternary ammonium salt from Akzo Nobel Corp., was mixed into a glass bottle (200ml). The bottles were vigorously shaken and then let stand to allow sands settle down. The sand grains immediately following agitation were fully distributed in water making stable slurry. After one hour, about half amount of sands settled down to the bottom while the other half was floating on the top.

#### Example 3

100 ml of water and 50 grams of 20/40 mesh ceramic proppants were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810, a capryl/capramidopropyl betaine from Degussa Corp., and 1 ml of a solution containing 20% Tegopren 6924, a di-quaternary polysiloxane from Degussa Corp., and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow proppants settle down. In the one containing Tegopren 6924 about 25% of proppants was floating on the top and the remaining 75% settled on the bottom. The volume of the 75% settled proppants was still significantly larger than the control one. When the bottles were tilted, the settled proppants in the bottle with straight water tended to move as individual

grains, while the settled proppants containing Tegopren 6924 tended to move as cohesive masses.

#### Example 4

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.1 ml of Tegopren 6924 and 0.1 ml of TEGO Betaine 810, were added and further added 2 wt% KCl. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. In the bottle containing Tegopren 6924, about 15% of sands was floating on the top and the remaining 85% settled on the bottom. The volume of the 85% settled sand was still significantly larger than the control one. When the bottles were tilted, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands containing Tegopren 6924 tended to move as cohesive masses.

#### Example 5

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. After thoroughly mixing the sands were separated from the liquid and dried at room temperature. The pre-hydrophobonized sands were mixed with 100ml water and shaken vigorously. In the bottle containing Tegopren 6924, about 40% of sands was floating on the top and the remaining 60% settled on the bottom. The volume of the 60% settled



sand was still significantly larger than the control one. When the bottles were tilted, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands containing Tegopren 6924 tended to move as cohesive masses.

#### Example 6

100 ml of water and 50 grams of coal particulates were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. The other bottle was used as control. In the bottle containing Tegopren 6924, about 45% of coal particulates was floating on the top and the remaining 55% settled on the bottom. The volume of the 55% settled coal particulates was about 15% smaller than the control one.

#### Example 7

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.03 ml of Maquat QSX, a quaternary silane compound characterized as triethoxysilyl soyapropyl dimonium chloride in butylene glycol, was added into one of the bottles. The other bottle was used as control. After being thoroughly mixed the liquid above the settled sand was discarded and replaced with same amount of water. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. In the bottle containing Maquat QSX, about 5% of sands was floating on the top and remain 95% settled on the bottom. The volume of the 95% settled sand was still significantly larger than the

control one. When the bottles were tilted, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands containing Maquat QSX tended to move as cohesive masses.

#### Example 8

100 ml of water and 50 grams of 20/40 mesh resin coated sands were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow resin coated sands settle down. The volume of settled sands containing Tegopren 6924 is about twice of that in the control one.

As mentioned above, the present invention is particularly useful in many applications in the petroleum industry as well as in other industries. Examples include various well service operations including hydraulic fracturing, gravel pack, wellbore cleanout and drilling, particulate transportation through pipe lines and sand blasting.

When used in a hydraulic fracturing operation, a large amount of proppants can effectively be transported into subterranean formation without using a viscosifier. It is not only cost-effective but also eliminates damage to the formation and proppant pack caused by polymer residues. An EHRC, for example a di-quaternary polysiloxane can be added to a water-based fracturing fluid containing proppants to make the slurry and then pumped into the formation during the proppant stage. Various aqueous fracturing fluids including water,



brine, linear polymer fluid, cross-linked polymer fluid and viscoelastic surfactant fluid can be used. It is particularly beneficial to use the slurry in so-called slick-water fracturing treatment. In conventional slick-water fracturing operations, due to the low viscosity of the fluid, only low concentration of proppants can be effectively pumped deep into a formation, and moreover the proppants tend to settle down on the bottom of the fracture, resulting in lower conductivity. With the composition of the present invention, high concentration of proppants can easily be pumped deep into a formation and the proppants are more evenly distributed in the fracture, leading to improved conductivity of the proppant pack. During the fracturing operation, the EHRC can be added on-the-fly. Optionally, one can use proppants already rendered extremely hydrophobic in the fracturing operation. Another benefit of the slurry of the present invention is that the fluid is readily re-useable after flow back from a well. This has great significance considering there is limited water supply in a number of places.

The present invention also provides a new method for preventing proppant flowback after a fracturing treatment. In field operations, proppants can be pumped into a formation using the composition of the present invention. Various aqueous fracturing fluid, for example water, brine, a linear polymer fluid, a cross-linked polymer fluid or a viscoelastic surfactant fluid can be used. Alternatively, a fluid medium containing an EHRC can be pumped into the formation following the proppant stage to mix with particulates already in the formation. The particulates in the slurry tend to move cohesively in contrast to conventional slurries under the same conditions. It is worth noting that the cohesiveness



among the proppant grains in the present slurry originates from hydrophobic interactions, instead of tackiness as described, for example in US Patent 6,047,772.

The slurry of the present invention is particularly useful in gravel-pack operations where sand slurry is normally pumped into a wellbore to prevent excessive amount of sands from flowing into the wellbore from the formation. The present method is cost effective and the sand pack formed has a high conductivity. Similarly, the slurry can also be used in so-called formation consolidation operations. In such an operation, a fluid containing an EHRC is injected into a formation to increase cohesiveness among sand grains to consolidate the formation and to reduce sand production.

In drilling operations, an EHRC can be added directly to a water-based drilling fluid. It is particularly useful when the EHRC is added to water or brine for use as a drilling fluid. During a drilling operation, the fluid forms slurry in situ with cuttings and transports the cuttings out of the wellbore. A gas such as nitrogen or carbon dioxide can be mixed with the slurry during drilling. Since it is not necessary to use polymers or clays to viscosify the fluid, there is much less formation damage. Moreover, the cuttings can be easily removed on the surface and the fluid becomes readily re-useable. Different formations including sandstone, carbonate, shale and coal seams can be drilled using the slurry of the present invention.

Similarly in wellbore cleanout operations, water or brine containing an EHRC can circulate in the wellbore and form slurry with debris in situ. The debris

is subsequently transported out of the wellbore as slurry. The fluid is readily re-useable after separation from the debris.

For transporting particulates through pipelines slurry can be prepared by mixing the ingredients and then pumping the slurry through the pipeline.

## CLAIMS:

1. An aqueous slurry composition comprising:
  - (a) water;
  - (b) particulates; and
  - (c) a chemical compound for rendering the surface of the particulates extremely hydrophobic.
2. The composition of claim 1, wherein the particulates are selected from the group consisting of sand, resin coated sand, ceramic, carbonate, bauxite, shale and coal particulates.
3. The composition of claim 1, wherein the particulates are subterranean formation particulates.
4. The composition of claim 1, wherein the chemical compound is selected from the group consisting of an organosilane, an organosiloxane, a fluoro-organosilane, a fluorro-organosiloxane and a fluoro-organic compound.
5. The composition of claim 1, wherein the chemical compound is an organosilane having the formula



wherein R is an organic radical having 1-50 carbon atoms, X is a halogen, alkoxy, acyloxy or amine and n has a value of 1-3.

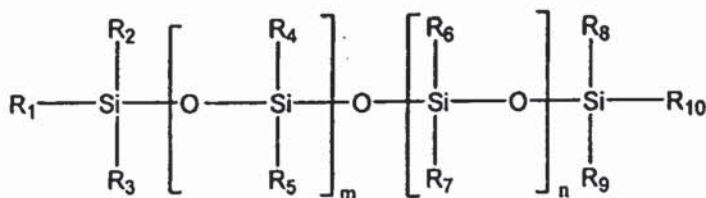
6. The composition of claim 5, wherein the organosilane is selected from the group consisting of:

CH<sub>3</sub>SiCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>,  
(C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>HSiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiCl, CH<sub>3</sub>SiBr<sub>3</sub>,



$(C_6H_5)SiBr$ ,  $(CH_3)_2SiBr_2$ ,  $(CH_3CH_2)_2SiBr_2$ ,  $(C_6H_5)_2SiBr$ ,  $(CH_3)_3SiBr$ ,  
 $CH_3HSiBr_2$ ,  $(CH_3)_2HSiBr$ ,  $Si(OCH_3)_4$ ,  $CH_3Si(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_3)_3$ ,  
 $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_3Si[O(CH_2)_3CH_3]_3$ ,  $CH_3CH_2Si(OCH_2CH_3)_3$ ,  
 $C_6H_5Si(OCH_3)_3$ ,  $C_6H_5CH_2Si(OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_3)_3$ ,  
 $(CH_3)_2Si(OCH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_2CH_3)_2$ ,  
 $(CH_3)_2Si[O(CH_2)_3CH_3]_2$ ,  $(CH_3CH_2)_2Si(OCH_2CH_3)_2$ ,  $(C_6H_5)_2Si(OCH_3)_2$ ,  
 $(C_6H_5CH_2)_2Si(OCH_3)_2$ ,  $(C_6H_5)_2Si(OCH_2CH_3)_2$ ,  $(CH_2=CH_2)Si(OCH_3)_2$ ,  
 $(CH_2=CHCH_2)_2Si(OCH_3)_2$ ,  $(CH_3)_3SiOCH_3$ ,  $CH_3HSi(OCH_3)_2$ ,  $(CH_3)_2HSi(OCH_3)$ ,  
 $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_2CH_2OCH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(CH_2=CH_2)_2Si(OCH_2CH_2OCH_3)_2$ ,  $(CH_2=CHCH_2)_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_2CH_2OCH_3)_2$ ,  $CH_3Si(CH_3COO)_3$ , methyltriethylchlorosilane,  
butyltrichlorosilane diphenyldichlorosilane, vinyltrichlorosilane,  
methyltrimethoxysilane, vinyltriethoxysilane, vinyltris(methoxyethoxy)silane,  
methacryloxypropyltrimethoxysilane, glycidoxypyltrimethoxysilane,  
aminopropyltriethoxysilane, divinyl-di-2-methoxysilane, ethyltributoxysilane,  
isobutyltrimethoxysilane, hexyltrimethoxysilane, n-octyltriethoxysilane,  
dihexyldimethoxysilane; trichloro-octadecylsilane, 3-  
(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride, 3-  
(trimethylethoxysilylpropyl)didecylmethyl ammonium chloride and triethoxysilyl  
soyapropyl dimonium chloride.

7. The composition of claim 1, wherein the chemical compound is an organo-siloxane having the formula



wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$ , represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $R_7$  represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and  $m$  and  $n$  are from 1 to 200.

8. The composition of claim 7, wherein the chemical compound is an organic betaine polysiloxane.

9. The composition of claim 8, wherein the chemical compound is an organic betaine polysiloxane, and the values of  $m$  and  $n$  are from 1 to 100.

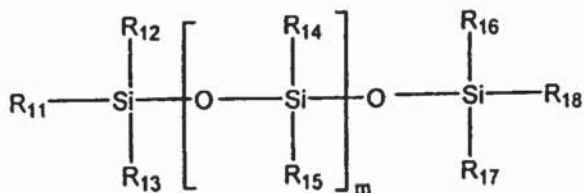
10. The composition of claim 9, wherein the chemical compound is an organic betaine polysiloxane, wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$  is a methyl group and the values of  $m$  and  $n$  are from 1 to 100.

11. The composition of claim 7, wherein the chemical compound is an organic quaternary polysiloxane.

12. The composition of claim 11, wherein the chemical compound is an organic quaternary polysiloxane, and the values of  $m$  and  $n$  are from 1 to 100.

13. The composition of claim 12, wherein the chemical compound is an organic quaternary polysiloxane, and each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$  is a methyl group and the values of  $m$  and  $n$  are from 1 to 100.

14. The composition of claim 1, wherein the chemical compound is an organo-siloxane having the formula



where  $\text{R}_{12}$  to  $\text{R}_{17}$  each represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_{11}$  and  $\text{R}_{18}$  each represents an organic betaine group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and  $m$  is 1 to 200.

15. The composition of claim 14, wherein the chemical compound is a di-betaine polysiloxane.
16. The composition of claim 15, wherein the chemical compound is a di-betaine polysiloxane and the values of  $m$  are from 1 to 100.
17. The composition of claim 16, wherein each of  $\text{R}_{12}$  to  $\text{R}_{17}$  represents a methyl group and the  $m$  is from 1 to 100.
18. The composition of claim 14, wherein the chemical compound is a di-quaternary polysiloxane.
19. The composition of claim 18, wherein the chemical compound is a di-quaternary polysiloxane, and the values of  $m$  are from 1 to 100.
20. The composition of claim 19, wherein each of  $\text{R}_{12}$  to  $\text{R}_{17}$  represents a methyl group and the  $m$  is from 10 to 100.
21. The composition of any one of claims 1 to 20 includes a gas.
22. The composition of claim 21, wherein the gas is selected from the group consisting of air, nitrogen, carbon dioxide, methane and mixtures thereof.



23. A method of producing an aqueous slurry composition comprising the step of mixing water, particulates and a chemical compound for rendering the surface of the particulates extremely hydrophobic.

24. The method of claim 23, wherein the particulates are selected from the group consisting of sand, resin coated sand, ceramic, carbonate, bauxite, shale and coal particulates.

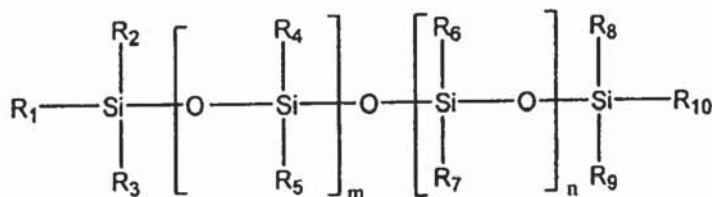
25. The method of claim 23, wherein the chemical compound is selected from the group consisting of an organosilane, an organosiloxane, a fluoro-organosilane, a fluoro-organosiloxane and a fluoro-organic compound.

26. The composition of claim 25, wherein the chemical compound is an organosilane having the formula



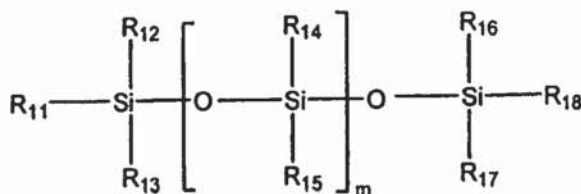
wherein R is an organic radical having 1-50 carbon atoms, X is a halogen, alkoxy, acyloxy or amine and n has a value of 1-3.

27. The composition of claim 25, wherein the chemical compound is an organo-polysiloxane having the formula



wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$ , represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $R_7$  represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and m and n are from 1 to 200.

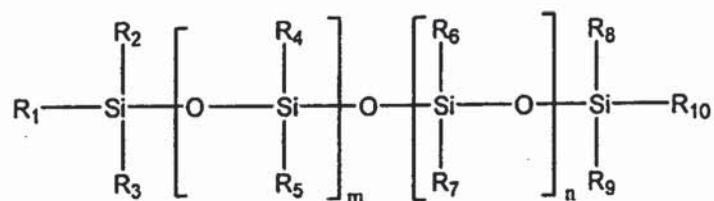
28. The composition of claim 27, wherein the particulates are sands.
29. The composition of claim 25, wherein the chemical compound is an organo-siloxane having the formula



where  $\text{R}_{12}$  to  $\text{R}_{17}$  each represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_{11}$  and  $\text{R}_{18}$  each represents an organic betaine group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and  $m$  is 1 to 200.

30. The composition of claim 29, wherein the particulates are sands.
31. The method of claim 23, including the step of subjecting the slurry composition to shear in the presence of a gas.
32. The method of claim 31, wherein the gas is selected from the group consisting of air, nitrogen, carbon dioxide, methane and mixtures thereof.
33. The method of claim 23, including the steps of contacting the particulate with a medium containing the chemical compound to render the particulate hydrophobic, separating the particulate from the medium; and blending the hydrophobic particulate with water.
34. The method of claim 33, including the step of subjecting the slurry composition to shear in the presence of a gas.
35. The method of claim 33, wherein the gas is selected from the group consisting of air, nitrogen, carbon dioxide, methane and mixtures thereof.

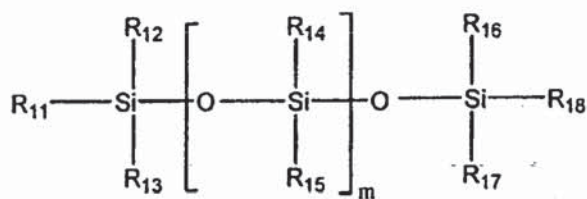
36. The composition of claim 33, wherein the chemical compound is an organo-polysiloxane having the formula



wherein each of R<sub>1</sub> to R<sub>6</sub> and R<sub>8</sub> to R<sub>10</sub>, represents an organic radical containing 1-6 carbon atoms, typically a methyl group, R<sub>7</sub> represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and m and n are from 1 to 200.

37. The composition of claim 36, wherein the particulates are sands.

38. The composition of claim 33, wherein the chemical compound is an organo-siloxane having the formula



where R<sub>12</sub> to R<sub>17</sub> each represents an organic radical containing 1-6 carbon atoms, typically a methyl group, R<sub>11</sub> and R<sub>18</sub> each represents an organic betaine group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and m is 1 to 200.

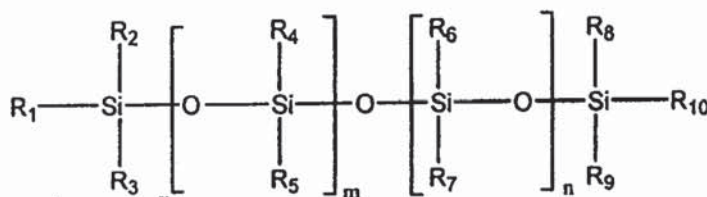
39. The composition of claim 38, wherein the particulates are sands.

40. A method of producing an aqueous slurry composition for a well service operation in various formations, comprising the step of mixing water, particulates



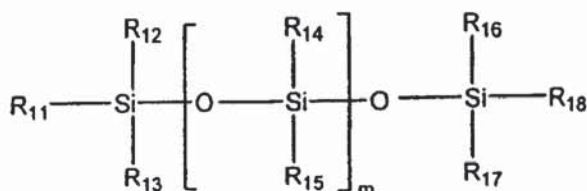
and a chemical compound for rendering the surface of the particulates extremely hydrophobic.

41. The well service operation in claim 40 is selected from the group consisting of hydraulic fracturing, drilling, completion and sand pack operation.
42. The method of claim 40, including the step of subjecting the slurry composition to shear in the presence of a gas.
43. The fluid in Claim 40 can be re-used after separated from the particulates.
44. The composition of claim 40, wherein the chemical compound is an organo-polysiloxane having the formula



wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$ , represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $R_7$  represents an organic betaine group for an organic betaine polysiloxane or an organic quaternary group for an organic quaternary polysiloxane, and  $m$  and  $n$  are from 1 to 200.

45. The composition of claim 40, wherein the chemical compound is an organo-siloxane having the formula



where  $R_{12}$  to  $R_{17}$  each represents an organic radical containing 1-6 carbon atoms, typically a methyl group,  $R_{11}$  and  $R_{18}$  each represents an organic betaine

group for a di-betaine polysiloxane or an organic quaternary group for a di-quaternary polysiloxane, and m is 1 to 200.

46. A method of producing an aqueous slurry composition for transporting particulates through a pipeline, comprising the step of mixing water, particulates and a chemical compound for rendering the surface of the particulates extremely hydrophobic, and pumping the slurry through the pipeline.

47. The composition of claim 46, wherein the particulates are sands.

48. The composition of claim 46, wherein the particulates are coal particulates.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CA2006/000705

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC: <i>C08L 83/04</i> (2006.01), <i>C09K8/68</i> (2006.01), <i>E21B 43/267</i> (2006.01) and <i>B01J2/30</i> (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC C09K8/00 (version 8.0) IPC C09K7/00 (versions 7.0 and earlier) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Canadian Patent Databases, WEST, Espacenet, Delphion/DWPI, SCOPUS, ACS Journals, Google Scholar		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA2423031 A1 (BJ SERVICES COMPANY) 01 January 2003 (01-01-2003) abstract; page 12, lines 21-29; page 20, line 15 to page 23, line 21; page 29, lines 20-23; examples 3-5	1, 2, 4, 5, 23-26
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X	CA1104804 A (UNION CARBIDE) 28 December 1978 (28-12-1978) page 4; example 1	1, 2, 4, 5, 23-26
X	US4454056 A (DEGUSSA) 12 June 1984 (12-06-1984) example 5	1, 2, 4, 5, 23-26
X	JP58146434 (NEOS KK) 01 September 1983 (01-09-1983) English abstract	1, 2, 4, 5, 23-26, 46, 48
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search July 14 2006 (14-07-2006)		Date of mailing of the international search report 25 August 2006 (25-08-2006)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001(819)953-2476		Authorized officer Yong-Huang Chen (819) 956-4113



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International application No.  
PCT/CA2006/000705

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CA2408052 (TRICAN WELL SERVICE) 08 November 2001 ( 08-11-2001 ) whole document	1-45

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Information on patent family members

International application No.  
PCT/CA2006/000705

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International application No.  
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(54) Title: **SLURRY COMPOSITIONS AND METHODS FOR MAKING SAME**

(57) Abstract: An aqueous slurry composition for use in industries such as the petroleum and pipeline industries includes a particulate, an aqueous liquid and a chemical compound that renders the particulate surface extremely hydrophobic. The slurry is produced by rendering the surface of the particulate extremely hydrophobic during or before making the slurry.

Preferred Proppants, LLC, Preferred Pipeline, LLC, Preferred Resin Sales, LLC, Preferred Resin of Genoa, LLC, Preferred Sands of Wisconsin, LLC, Ex. 1003, p. 482 of 1051



WO 2007/033489 A2

## **Slurry Compositions and the Methods for Making Same**

### **BACKGROUND OF THE INVENTION**

#### **Field of the Invention**

This invention relates to an aqueous slurry composition and to a method of making such a composition.

#### **Discussion of the Prior Art**

Aqueous particulate slurries are commonly used or encountered in many industries including the petroleum, pipeline, construction and cleaning industries. Slurries are mixtures normally comprising particulates and an aqueous medium and play an essential role in many industrial operations. For example, slurries are used for transporting particulates from one location to another at different distances either above ground, or from the surface to a subterranean formation or from a subterranean formation to the surface. The most commonly used particulates include sand, ceramic particulates, carbonate particulates, glass spheres, bauxite (aluminum oxide) particulates, resin coated particulates and coal particulates. The particulate sizes normally range from about 10 to about 100 US mesh, and the particulate densities are significantly higher than the density of water. For example, the density of sand is at about  $2.6 \text{ g/cm}^3$  while the density of water is  $1 \text{ g/cm}^3$ . Sand is by far the most commonly used particulate.

To make relatively stable slurry, particulates must be suspended in a liquid medium for a lengthy period at static or/and dynamic conditions. Convention wisdom tells us that the viscosity or viscoelasticity of the liquid medium must be sufficiently high to be able to suspend particulates. The most commonly used



method for increasing viscosity or viscoelasticity of an aqueous liquid is by adding a viscosifier, for example, a natural or synthetic polymer or a viscoelastic surfactant to the liquid medium. It is not unusual that a polymer is used with a foaming agent in order to take advantage of both viscoelastic and foaming properties. However, the use of polymers in slurries increases cost and results in operational difficulties. In particular applications, for example, hydraulic fracturing of subterranean formations, the use of polymers in slurry impedes oil and gas production due to large amounts of residue left in the formation. As for viscoelastic surfactants, although they have fewer residues compared to normal polymers, their cost is usually much higher. In many other applications such as gravel-pack, well completion and sand transportation through pipelines, it is highly desirable to make stable particulate slurry without using a viscosifier.

Hydraulic fracturing operations are used extensively in the petroleum industry to enhance oil and gas production. In hydraulic fracturing, a fracturing fluid is injected through a wellbore into a subterranean formation at a pressure sufficient to initiate fractures, which increase oil and gas production. Frequently, particulates, called proppants, are suspended in the fracturing fluid and transported into fractures as slurry. Proppants include sands, ceramic particulates, bauxite particulates, resin coated sands and other particulates known in the industry. Among them sand is by far the most commonly used proppant.

Fracturing fluids in common use include water-based as well as hydrocarbon-based fluids. In water-based fracturing fluids, a polymer or



viscoelastic surfactant is normally employed to increase the viscoelasticity of the fluid. In most cases the viscoelastic property of the fluids is essential for transporting proppants deep into a formation. At the last stage of the fracturing treatment, fracturing fluid flows back to the surface and the proppants are left in the fracture forming a proppant pack to prevent the fracture from closing after pressure is released. A proppant-filled fracture provides a highly conductive channel that allows oil and/or gas to seep through more efficiently to the wellbore. The conductivity of the proppant pack plays a dominant role in production enhancement. Polymer residues from fracturing fluids are known to greatly reduce the conductivity of the proppant pack.

Compared to polymeric viscosifiers, viscoelastic surfactants cause less damage to formations and proppant packs. However, they are much more expensive.

Accordingly, a need exists for a composition for efficiently transporting proppants deep into a formation at low cost while at the same time causing little damage to the formation and proppant pack. Grain size, concentration, shape and the packing pattern of proppants are also important factors in determining the conductivity. Despite extensive research in recent years, limited progress has been achieved to maximize the conductivity of a proppant pack in a fracture. Therefore, a need exists for making a composition for use in a proppant pack with improved conductivity.

Proppant flowback after fracturing treatments has long been plaguing the petroleum industry. Flowback reduces the amount of proppants in the formation

leading to a less conductive fracture. As disclosed, for example in US Patent 6,047,772, various methods have been tried to solve the flowback problem. In one method, resins are used to coat the proppant and make them very tacky. In doing so, the proppant grains tend to stick together reducing flowback. This method is not only expensive, but the tacky resins introduced in the proppant pack tend to reduce its conductivity. Therefore, there is a need for a composition and method for making slurry, which can form a stable proppant pack resisting proppant flowback, while at the same time has a high conductivity.

When drilling subterranean formations for oil and gas, aqueous-based drilling fluids are normally used. During drilling large amounts of particles, called cuttings are generated. Cuttings have different sizes ranging from fines to pebbles. The drilling fluid is circulated through the wellbore to make slurry with the cuttings in situ and transports them out of wellbore. In most cases, polymers as well as clays are added to the drilling fluids to increase their viscosity/viscoelasticity in order to transport the cuttings efficiently. However, polymers as well as clay fines, can easily penetrate into pores or thin fractures in a formation and reduce formation permeability significantly, especially near wellbore. Reduced formation permeability impedes oil and/or gas production. Therefore it is highly desirable to provide a drilling fluid that can make stable slurry in situ with the cuttings and transport them out of the wellbore, while causing little formation damage.

The escalating price of oil and its alarming depletion rate have caused people to consider using coal as an oil substitute. Several factors have slowed

the substitution of coal for oil. One factor is the difficulty in transporting coal cost-effectively over long distance through pipelines. It is therefore highly desirable to provide a composition for making coal slurry which is stable, highly fluid and cost-effective to transport.

In oil sand operation massive amount of sands are left after oil is stripped from the sand surface. Finding a more cost effective way to transport sands efficiently over distance through pipelines has long been required in the industry. Thus, a composition and a method for making stable and highly fluid sand slurries at low cost would be quite useful.

#### SUMMARY OF THE INVENTION

Accordingly, one aspect of the present invention relates to an aqueous slurry compositions, which can be used to form a stable, highly conductive proppant pack, for efficiently transporting proppants into a subterranean formation, and for use in transporting drilling cuttings, coal particulates and sands.

The invention also relates to an aqueous slurry composition comprising particulates, an aqueous liquid and a chemical compound that renders the surface of the particulates extremely hydrophobic, and the method of making such slurry composition.

The invention still further relates to a slurry composition comprising particulates, an aqueous liquid, a chemical compound that renders the surface of the particulates extremely hydrophobic and a gas, and the method of making such slurry composition.



The invention also relates to a slurry composition comprising particulates, an aqueous liquid, a chemical compound that renders the surface of the particulates extremely hydrophobic and a surfactant.

The invention also relates to a slurry composition comprising particulates, an aqueous liquid, a chemical compound that renders the surface of the particulates extremely hydrophobic, a surfactant and a gas, and the method of making such slurry composition. The invention also relates to a method of making an aqueous slurry composition comprising steps of first rendering the particulate surface extremely hydrophobic and then mixing the treated particulates with an aqueous liquid, or an aqueous liquid containing a gas.

The invention in another aspect also relates to methods of making the aqueous slurry compositions, including for various applications including hydraulic fracturing, drilling, gravel-pack, transportation through pipelines, blasting and tunneling.

#### DETAILED DESCRIPTION OF THE INVENTION

It is discovered in the present invention that when the surface of particulates according to the invention become extremely hydrophobic, a slurry made with such particulates has several novel properties. For example, particulates tend to move cohesively instead as individual grains; the bulk volume of settled particulates tend to be significantly greater than in a slurry formed by convention methods under the same conditions; the particulate pack formed tends to have high conductivity and can be easily dewatered, and the slurry tends to be fluid and stable at static or dynamic conditions without using a

viscosifier. The larger bulk volume of the particulate pack indicates a larger porosity and therefore higher conductivity. This is particularly beneficial for improving fracturing treatment, since, as mentioned above, the conductivity of the proppant pack is the dominant property affecting fracturing treatments. The extremely hydrophobic surface of the particulate further reduces the dragging force exerted by the fluid and makes it more difficult for proppants to be carried away by the fluid once the particulates become completely settled. This is particularly beneficial for minimizing proppant flowback after fracturing treatments, leading to increased proppant conductivity. In conventional slurries, viscosity or viscoelasticity of the liquid plays a dominant role while the interfacial interactions between the particulate surface and the liquid play negligible role. However, it is discovered in the present invention that when the surface of the particulate becomes extremely hydrophobic, the interfacial interactions between the surface and the liquid become increasingly important.

In general, the interfacial interactions between a solid substrate and a liquid mainly depend on the surface properties of the solid and the surface tension of the liquid. Normally the macroscopic properties of a solid surface can be characterized by observing the shape of a liquid droplet on the solid substrate, which is the result of free energy of the surface, as well as the free energy of the liquid. When a liquid does not completely wet a surface, it forms an angle  $\theta$ , which is known as the contact angle. The contact angle is the angle formed between a solid substrate and the tangent line at the point of contact between a liquid droplet and the solid substrate. The contact angle can be measured directly



on macroscopic, smooth, nonporous, planar solid substrates by merely placing a droplet of the liquid or solution on the solid substrate and determining the contact angle by any of number of techniques. The values of contact angles between many solids and aqueous liquid are provided in various books and scientific publications, which will be known to those skilled in the art. It is known that the majority of naturally occurring minerals are hydrophilic. It is also known that certain hydrocarbon compounds, for example, some conventional quaternary surfactants, amine surfactants and cationic polyacrylamides can be used to reduce the surface energy of certain particulates and make the particulate surface less hydrophilic or more hydrophobic. However, the "hydrophobicity" imparted by such compounds is not high enough to be included in the term of "extremely hydrophobic" as in the case of the present invention. In the present invention, "extremely hydrophobic" means that the contact angle of water on the solid substrate is greater than about  $90^\circ$ . At such high contact angles, water does not wet the surface of the solid and instead contracts on the solid surface and forms beads. The chemical compounds that can render a particulate surface extremely hydrophobic are referred as "extremely hydrophobic rendering compounds" (EHRC) for the sake of simplicity. EHRC normally are those compounds that contain organosilane or organosiloxane groups. Because of such groups, EHRC are able to impart hydrophobicity to solid surface to a level that conventional hydrocarbon surfactants or polymers are not able to achieve. These compounds are known to render many inorganic solid surfaces extremely hydrophobic.



Slurries according to the invention can be made on the ground or in situ in a subterranean formation. Such slurries have numerous applications in many industries, including for (a) transporting particulates over various distances, either on the surface of the ground, from the surface to a subterranean formation or from a subterranean formation to the surface, and (b) well service operations including stimulation, drilling, completion, gravel-pack, controlling sand production and the like.

Furthermore, a gas can be mixed into the slurries of the invention. Suitable gases for use in the slurry include air, carbon dioxide, nitrogen, methane and mixtures thereof. The gas can be introduced into the slurries during preparation thereof. For example, when the slurry is pumped through a pipe, gas such as nitrogen can be introduced into the slurry, or gas such as air can be simply mixed into the slurry through a sufficient rate of agitation.

In the present invention, "aqueous liquids" means water, salt solutions, water containing an alcohol or other organic solvents. It should be understood that the additives other than water in the aqueous liquid are used in amounts or in a manner that does not adversely affect the present invention. One can also add polymers into the aqueous liquid. For example, in so-called slick-water fracturing operations, a small amount of polymer is normally added into an aqueous liquid to reduce friction pressure during pumping.

The size of particulates in compositions according to the invention is about 10-100 US mesh, which is about 150 to 1400  $\mu\text{m}$ . It should be understood that the size distribution of particulates can be narrow or wide. Suitable particulates

include sands, ceramic particulates, glass beads, bauxite particulates, resin coated sands, carbonates and coal particulates.

It is known that many organosilicon compounds including organosiloxane, organosilane, fluoro-organosiloxane and fluoro-organosilane compounds are commonly used to render various surfaces extremely hydrophobic. For example, see United States patent nos. 4,537,595; 5,240,760; 5,798,144; 6,323,268; 6,403,163; 6,524,597 and 6,830,811. It is normally not difficult for those skilled in the art to find suitable organosilicon compounds to render a solid surface extremely hydrophobic. However, it discovered in the present invention that when the surfaces of particulates are rendered extremely hydrophobic in aqueous slurry, the slurry exhibits novel properties which are not seen in conventional aqueous slurry. For example, particulates tend to move cohesively instead as individual grains; the bulk volume of settled particulates tend to be significantly greater than in a slurry formed by convention methods under the same conditions; the particulate pack formed tends to have high conductivity and be easily dewatered, and the slurry tends to be fluid and stable at static or dynamic conditions without using a viscosifier.

Organosilanes are compounds containing silicon to carbon bonds. Organosiloxanes are compounds containing Si-O-Si bonds. Polysiloxanes are compounds in which the elements silicon and oxygen alternate in the molecular skeleton, i.e., Si-O-Si bonds are repeated. The simplest polysiloxanes are polydimethylsiloxanes. Polysiloxane compounds can be modified by various organic substitutes having different numbers of carbons, which may contain N, S,



or P moieties that impart desired characteristics. For example, cationic polysiloxanes are compounds in which one or two organic cationic groups are attached to the polysiloxane chain, either at the middle or the end. Normally the organic cationic group contains at least 10 carbons and may contain a hydroxyl group or other functional groups containing N or O. The most common organic cationic groups are alkyl amine derivatives including secondary, tertiary and quaternary amines (for example, quaternary polysiloxanes including, quaternary polysiloxanes including mono- as well as di-quaternary polysiloxanes, amido quaternary polysiloxanes, imidazoline quaternary polysiloxanes and carboxy quaternary polysiloxanes).

Similarly, the polysiloxane can be modified by organic amphoteric groups, where one or two organic amphoteric groups are attached to the polysiloxane chain, either at the middle or the end, and include betaine-polysiloxanes and phosphobetaine polysiloxanes.

Similarly, the polysiloxane can be modified by organic anionic groups, where one or two organic anionic groups are attached to the polysiloxane chain, either at the middle or the end, including sulfate polysiloxanes, phosphate polysiloxanes, carboxylate polysiloxanes, sulfonate polysiloxanes, thiosulfate polysiloxanes. The organosiloxane compounds also include alkylsiloxanes including hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane. The organosilane compounds include



alkylchlorosilane, for example methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, octadecyltrichlorosilane; alkyl-alkoxysilane compounds, for example methyl-, propyl-, isobutyl- and octyltrialkoxysilanes, and fluoro-organosilane compounds, for example, 2-(n-perfluoro-octyl)-ethyltriethoxysilane, and perfluoro-octyldimethyl chlorosilane.

Other types of chemical compounds, which are not organosilicon compounds, which can be used to render particulate surface extremely hydrophobic are certain fluoro-substituted compounds, for example certain fluoro-organic compounds.

Further information regarding organosilicon compounds can be found in *Silicone Surfactants* (Randal M. Hill, 1999) and the references therein, and in United States Patent Nos. 4,046,795; 4,537,595; 4,564,456; 4,689,085; 4,960,845; 5,098,979; 5,149,765; 5,209,775; 5,240,760; 5,256,805; 5,359,104; 6,132,638 and 6,830,811 and Canadian Patent No. 2,213,168.

Organosilanes can be represented by the formula



wherein R is an organic radical having 1-50 carbon atoms that may possess functionality containing N, S, or P moieties that imparts desired characteristics, X is a halogen, alkoxy, acyloxy or amine and n has a value of 0-3. Examples of suitable organosilanes include:

CH<sub>3</sub>SiCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>HSiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiCl, CH<sub>3</sub>SiBr<sub>3</sub>,

$(C_6H_5)_3SiBr_3$ ,  $(CH_3)_2SiBr_2$ ,  $(CH_3CH_2)_2SiBr_2$ ,  $(C_6H_5)_2SiBr_2$ ,  $(CH_3)_3SiBr$ ,  $CH_3HSiBr_2$ ,  
 $(CH_3)_2HSiBr$ ,  $Si(OCH_3)_4$ ,  $CH_3Si(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_3)_3$ ,  
 $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_3Si[O(CH_2)_3CH_3]_3$ ,  $CH_3CH_2Si(OCH_2CH_3)_3$ ,  
 $C_6H_5Si(OCH_3)_3$ ,  $C_6H_5CH_2Si(OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_3)_3$ ,  
 $(CH_3)_2Si(OCH_3)_2$ ,  $(CH_2=CH)Si(CH_3)_2Cl$ ,  $(CH_3)_2Si(OCH_2CH_3)_2$ ,  
 $(CH_3)_2Si(OCH_2CH_2CH_3)_2$ ,  $(CH_3)_2Si[O(CH_2)_3CH_3]_2$ ,  $(CH_3CH_2)_2Si(OCH_2CH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_3)_2$ ,  $(C_6H_5CH_2)_2Si(OCH_3)_2$ ,  $(C_6H_5)_2Si(OCH_2CH_3)_2$ ,  
 $(CH_2=CH)_2Si(OCH_3)_2$ ,  $(CH_2=CHCH_2)_2Si(OCH_3)_2$ ,  $(CH_3)_3SiOCH_3$ ,  $CH_3HSi(OCH_3)_2$ ,  
 $(CH_3)_2HSi(OCH_3)$ ,  $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_2CH_2OCH_3)_2$ ,  $(CH_3)_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(CH_2=CH)_2Si(OCH_2CH_2OCH_3)_2$ ,  $(CH_2=CHCH_2)_2Si(OCH_2CH_2OCH_3)_2$ ,  
 $(C_6H_5)_2Si(OCH_2CH_2OCH_3)_2$ ,  $CH_3Si(CH_3COO)_3$ , 3-aminotriethoxysilane,  
 methyldiethylchlorosilane, butyltrichlorosilane, diphenyldichlorosilane,  
 vinyltrichlorosilane, methyltrimethoxysilane, vinyltriethoxysilane,  
 vinyltris(methoxyethoxy)silane, methacryloxypropyltrimethoxysilane,  
 glycidoxypropyltrimethoxysilane, aminopropyltriethoxysilane, divinyl-di-2-  
 methoxysilane, ethyltributoxysilane, isobutyltrimethoxysilane,  
 hexyltrimethoxysilane, n-octyltriethoxysilane, dihexyldimethoxysilane,  
 octadecyltrichlorosilane, octadecyltrimethoxysilane,  
 octadecyldimethylchlorosilane, octadecyldimethylmethoxysilane and quaternary  
 ammonium silanes including 3-(trimethoxysilyl)propyldimethyloctadecyl  
 ammonium chloride, 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium  
 bromide, 3-(trimethylethoxysilylpropyl)didecylmethyl ammonium chloride,

triethoxysilyl soyapropyl dimonium chloride, 3-

(trimethylethoxysilylpropyl)didecylmethyl ammonium bromide, 3-

(trimethylethoxysilylpropyl)didecylmethyl ammonium bromide, triethoxysilyl

soyapropyl dimonium bromide,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_5)_3\text{Cl}^-$ ,

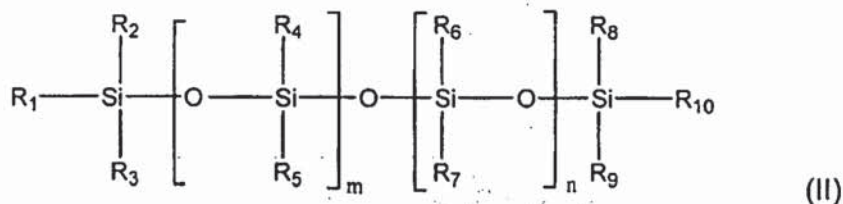
$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{CH}_3)_3\text{Cl}^-$ ,

$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_{13})_3\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_4\text{H}_9\text{Cl}^-$ ,

$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OHCl}^-$ ,

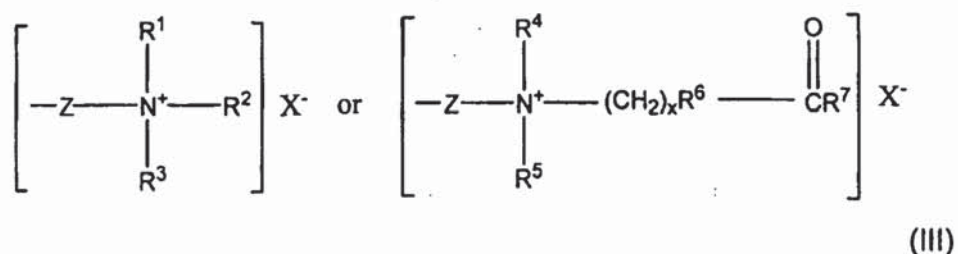
$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{C}_2\text{H}_5)_3\text{Cl}^-$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ .

Among different organosiloxane compounds which are useful for the present invention, polysiloxanes modified with organic amphoteric or cationic groups including organic betaine polysiloxanes and organic quaternary polysiloxanes are examples. One type of betaine polysiloxane or quaternary polysiloxane is represented by the formula



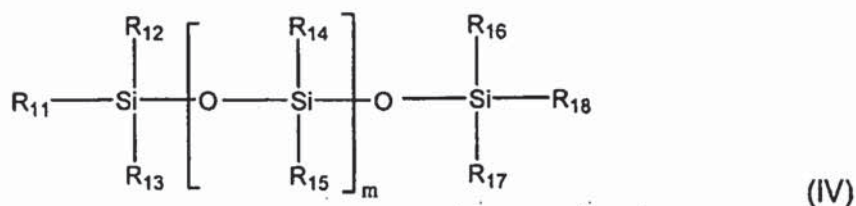
wherein each of the groups  $\text{R}_1$  to  $\text{R}_6$ , and  $\text{R}_8$  to  $\text{R}_{10}$  represents an alkyl containing 1-6 carbon atoms, typically a methyl group,  $\text{R}_7$  represents an organic betaine group for betaine polysiloxane, or an organic quaternary group for quaternary polysiloxane, and have different numbers of carbon atoms, and may contain a hydroxyl group or other functional groups containing N, P or S, and m and n are from 1 to 200. For example, one type of quaternary polysiloxanes is when  $\text{R}_7$  is represented by the group



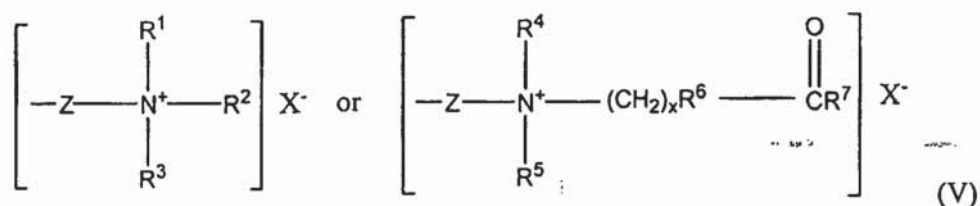


wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  are alkyl groups with 1 to 22 carbon atoms or alkenyl groups with 2 to 22 carbon atoms.  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^7$  are alkyl groups with 1 to 22 carbon atoms or alkenyl groups with 2 to 22 carbon atoms;  $\text{R}^6$  is  $-\text{O}-$  or the  $\text{NR}^8$  group,  $\text{R}^8$  being an alkyl or hydroxyalkyl group with 1 to 4 carbon atoms or a hydrogen group; Z is a bivalent hydrocarbon group with at least 4 carbon atoms, which may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group; x is 2 to 4; The  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^7$  may be the same or the different, and  $\text{X}^-$  is an inorganic or organic anion including  $\text{Cl}^-$  and  $\text{CH}_3\text{COO}^-$ . Examples of organic quaternary groups include  $[\text{R}-\text{N}^+(\text{CH}_3)_2-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{O}-(\text{CH}_2)_3-]$  ( $\text{CH}_3\text{COO}^-$ ), wherein R is an alkyl group containing from 1-22 carbons or an benzyl radical and  $\text{CH}_3\text{COO}^-$  an anion. Examples of organic betaine include  $-(\text{CH}_2)_3-\text{O}-\text{CH}_2\text{CH}(\text{OH})(\text{CH}_2)-\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ . Such compounds are commercial available. Betaine polysiloxane copolyol is one of examples. It should be understood that cationic polysiloxanes include compounds represented by formula (II), wherein  $\text{R}_7$  represents other organic amine derivatives including organic primary, secondary and tertiary amines.

Other example of organo-modified polysiloxanes include di-betaine polysiloxanes and di-quaternary polysiloxanes, which can be represented by the formula



wherein the groups  $\text{R}_{12}$  to  $\text{R}_{17}$  each represents an alkyl containing 1-6 carbon atoms, typically a methyl group, both  $\text{R}_{11}$  and  $\text{R}_{18}$  group represent an organic betaine group for di-betaine polysiloxanes or an organic quaternary group for di-quaternary, and have different numbers of carbon atoms and may contain a hydroxyl group or other functional groups containing N, P or S, and  $m$  is from 1 to 200. For example, one type of di-quaternary polysiloxanes is when  $\text{R}_{11}$  and  $\text{R}_{18}$  are represented by the group



wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{Z}$ ,  $\text{X}^-$  and  $x$  are the same as defined above.

Such compounds are commercially available. Quaternium 80 (INCI) is one of the commercial examples.

It should be appreciated by those skilled in the art that cationic polysiloxanes include compounds represented by formula (III), wherein  $\text{R}_{11}$  and  $\text{R}_{18}$  represents other organic amine derivatives including organic primary, secondary and tertiary amines. It should be apparent to those skilled in the art that there are different mono- and di-quaternary polysiloxanes, mono- and di-betaine polysiloxanes and other organo-modified polysiloxane compounds which

can be used to render the solid surfaces extremely hydrophobic and are useful in the present invention. These compounds are widely used in personal care and other products, for example as discussed in United States patent nos.

4,054,161; 4,654,161; 4,891,166; 4,898,957; 4,933,327; 5,166,297; 5,235,082; 5,306,434; 5,474,835; 5,616,758; 5,798,144; 6,277,361, 6,482,969, 6,323,268 and 6,696,052.

Another example of organosilicon compounds which can be used in the composition of the present invention are fluoro-organosilane or fluoro-organosiloxane compounds in which at least part of the organic radicals in the silane or siloxane compounds are fluorinated. Suitable examples are fluorinated chlorosilanes or fluorinated alkoxysilanes including 2-(n-perfluoro-octyl)ethyltriethoxysilane, perfluoro-octyldimethylchlorosilane,  $-(CF_3CH_2CH_2)_2Si(OCH_3)_2$ ,  $CF_3CH_2CH_2Si(OCH_3)_3$ ,  $(CF_3CH_2CH_2)_2Si(OCH_2CH_2OCH_3)_2$  and  $CF_3CH_2CH_2Si(OCH_2CH_2OCH_3)_3$  and  $(CH_3O)_3Si(CH_2)_3N^+(CH_3)_2(CH_2)_3NHC(O)(CF_2)_6CF_3Cl^-$ . Other compounds which can be used, but less preferable, are fluoro-substituted compounds, which are not organic silicon compounds, for example, certain fluoro-organic compounds.

It is understood that the particulate surfaces can be hydrophobized either by forming covalent bonds between the particulate surfaces and an EHRC or by adsorption of an EHRC on the particulate surfaces. For example, it is known that chlorosilanes and alkoxysilanes, which usually undergo hydrolysis in aqueous medium under suitable conditions, are used to modify surface through forming covalent bonds. Following hydrolysis, reactive silanol groups are formed, which



can condense with other silanol groups, for example, those on the surface of siliceous materials, to form covalent bonds. For example, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, their alkoxy derivatives can be used to render glass surface extremely hydrophobic through forming covalent bonds with the glass surfaces. It has been observed that polysiloxanes including various organic modified derivatives tend to have little tendency to hydrolysis under normal conditions. It is believed that they modify the surfaces predominantly by adsorption on the solid surfaces. It is common that solid surfaces, especially inorganic solid surfaces, in an aqueous medium possess charges, either negative or positive, which is influenced significantly by the pH of the aqueous medium. Organic substitutes on polysiloxane molecule, especially ionic ones having charges opposite to those on the solid surface, enhance significantly the adsorption of polysiloxanes on the solid surfaces. For example, a cationic polysiloxane can readily adsorb on sand surface in an aqueous liquid with neutral pH, at which the sand surface possesses negative charges. Similarly, an anionic polysiloxane, for example, a sulfonate polysiloxane tend to adsorb to a carbonate surface in an aqueous liquid more easily at neutral pH.

Slurries according to the present invention can be prepared, for example, by mixing an aqueous liquid with particulates and an EHRC, using conventional mixing method with a sufficient amount of shear. Alternatively, the particulates can be first treated by contacting the particulates with a fluid medium containing an EHRC to render the particulate surfaces extremely hydrophobic and then separating the particulates from the medium. The fluid medium can be a liquid or

a gas. The pre-hydrophobized particulates can later be used to make a slurry. In either case, a gas, including air, nitrogen, carbon dioxide, methane and mixtures thereof, can also be mixed into the slurries under agitation. Water is the most preferred aqueous liquid for making the slurry.

It is found in the present invention that adding suitable conventional hydrocarbon surfactants into the slurry composition is also useful. It should be understood that the surfactants should be added to the slurry at concentrations and in a manner which would not adversely affect the slurry. For example, when a surfactant is added to the slurries, one should try to avoid forming insoluble precipitates with the EHRC, or changing greatly the wettability of the particulate surface, or greatly reducing the surface tension of the aqueous liquid. For example, mixing cationic polysiloxane with an anionic hydrocarbon-surfactant, or vice versa, is normally not preferred, due to the tendency of causing undesired precipitations. Instead, when a cationic polysiloxane is used a cationic or an amphoteric hydrocarbon surfactant is more preferred. Similarly, when an anionic polysiloxane is used, an anionic surfactant or an amphoteric hydrocarbon surfactant is more preferred. Principles about surfactant compatibility are known to those skilled in the art. Also a very low surface tension of the aqueous liquid is not desirable. When the surface tension of the liquid is too low, more water can be added or some of the aqueous fluid containing surfactants can be replaced with water.

The slurries can be prepared on surface (above ground) or in a subterranean formation where the particulates, an aqueous fluid, and an EHRC,



for example a di-quaternary polysiloxane, are mixed in situ. Examples of situations where in situ mixing is used include drilling and wellbore cleanout operations. Alternatively, the particulates can be first mixed with a liquid in which an EHRC is dispersed or dissolved and then the particulates separated from the liquid or dried. The thus treated particulates can subsequently be used to make the slurry. Various proppants including sands, ceramic particulates or resin coated sands can be treated according to the present invention during manufacturing process. The thus prepared hydrophobic particulates can be used as proppants in fracturing operations. Depending on the amount and size of the particulates in the slurry, a wide range of EHRC concentration can be used to render the particulate surface extremely hydrophobic. Usually the amount of EHRC added is very small and has no apparent effect on the viscosity of the liquid to which it is added. For example, the concentration of EHRC in the slurry can be as low as a few ppm to hundreds of ppm. In most applications, it is unnecessary to add EHRC in an amount larger than 1 percent of the total liquid.

The following examples serve to illustrate the concepts of the present invention.

#### Example 1

50 ml of water and 50 grams of 20/40 mesh fracturing sands were added into each of two glass bottles (200ml). 0.5 ml of Tegopren 6923, a di-quaternary polydimethylsiloxane from Degussa Corp., was added into one of the bottles and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the



two bottles were compared. In the bottle containing Tegopren 6923, the volume of the settled sands was about 40 percent greater than the one without, and the sands are more fluid. When the bottles were tilted slowly, the settled sands in the control tended to move as individual sand grains, while the settled sands containing Tegopren 6923 tended to move as cohesive masses.

#### Example 2

50 ml water, 50 grams of 20/40 mesh fracturing sands, 0.5 ml of Tegopren 6923 and 0.1 ml of Aquard 18-50, C18-trimethylammonium chloride, a cationic hydrocarbon surfactant from Akzo Nobel Corp., was mixed into a glass bottle (200ml). The bottles were vigorously shaken and then let stand to allow sands settle down. All sands settled down to the bottom immediately in the control bottle. In the bottle containing Tegopren 6923, the sands immediately following agitation were fully distributed in the water making a stable slurry. After one hour, about half amount of sands settled on the bottom while the other half was floating on the top.

#### Example 3

100 ml of water and 50 grams of 20/40 mesh ceramic proppants were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810, capryl/capramidopropyl betaine, an amphoteric hydrocarbon surfactant from Degussa Corp., and 1 ml of a solution containing 20% Tegopren 6924, a di-quaternary polydimethylsiloxane from Degussa Corp., and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were vigorously shaken and then let stand to

allow proppants settle down. All proppants settled down to the bottom immediately in the control bottle. In the one containing Tegopren 6924 about 25% of proppants was floating on the top and the remaining 75% settled on the bottom, while the volume of the 75% settled proppants was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled proppants in the bottle with straight water tended to move as individual grains, while the settled proppants in the one containing Tegopren 6924 tended to move as cohesive masses.

#### Example 4

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.1 ml of Tegopren 6924 and 0.1 ml of TEGO Betaine 810, were added and further added 2 wt% KCl. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. All sands settled down to the bottom immediately in the control bottle. In the bottle containing Tegopren 6924, about 15% of sands was floating on the top and the remaining 85% settled on the bottom, while the volume of the 85% settled sand was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands in the one containing Tegopren 6924 tended to move as cohesive masses.

#### Example 5

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. After thoroughly mixing the sands were separated from the liquid and dried at room temperature. The pre-hydrophobized sands were mixed with 100ml water and shaken vigorously. All sands settled down to the bottom immediately in the control bottle. In the bottle containing pre-hydrophobized sands, about 40% of sands was floating on the top and the remaining 60% settled on the bottom, while the volume of the 60% settled sand was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled sands in the bottle with straight water tended to move as individual grains, while the settled pre-hydrophobized sands tended to move as cohesive masses.

#### Example 6

100 ml of water and 50 grams of coal particulates were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow coal particulates settle down. The coal particulates in the control bottle settled down immediately. In the bottle containing Tegopren 6924, about 45% of coal particulates was floating on the top and the remaining 55% settled on the bottom, while the volume of the



55% settled coal particulates was about only 15% smaller than the volume of 100% of the coal particles in the control one.

#### Example 7

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.03 ml of Maquat QSX, a quaternary silane compound characterized as triethoxysilyl soyapropyl dimonium chloride in butylene glycol, was added into one of the bottles. The other bottle was used as control. After being thoroughly mixed the liquid above the settled sand in the one containing Maquat QSX was discarded and replaced with same amount of water. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. All sands settled down to the bottom immediately in the control bottle. In the bottle containing Maquat QSX, about 5% of sands was floating on the top and remaining 95% settled on the bottom, while the volume of the 95% settled sand was still significantly larger than the control one. When the bottles were tilted slowly, the settled sands in the control bottle tended to move as individual grains, while the settled sands in the one containing Maquat QSX tended to move as cohesive masses.

#### Example 8

100 ml of water and 50 grams of 20/40 mesh resin coated sands were added into each of two glass bottles (200ml). 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were

vigorously shaken and then let stand to allow resin coated sands settle down. All resin coated sands settled down to the bottom immediately in the control bottle. In the bottle containing Tegopren 6924, about 15% of the resin coated sands was floating on the top and the remaining 85% settled on the bottom, while the volume of the 85% settled sand was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands in the one containing Tegopren 6924 tended to move as cohesive masses.

#### Example 9

50 gram of 30/50 mesh fracturing sands were mixed with 10 ml of silicone oil (polydimethylsiloxane) of viscosity of 20 cp and left on filter paper at room temperature for 24 hours. 10 gram of the pre-hydrophobized sands and 50 ml of water is mixed into glass bottle (200 ml). 10 gram of untreated sands into 50 ml of water was used as control. The bottles were vigorously shaken and then let stand to allow resin sands settle down. All sands in the control bottle settled down to the bottom immediately. In the bottle containing pre-hydrophobized sands, a small amount of sands was floating on the top of water. The volume of settled pre-treated sands is significant larger than that in the control one. When the bottles were tilted slowly, the settled sands in the control bottle tended to move as individual grains, while the settled pre-hydrophobized sands tended to move as cohesive masses.

#### Example 10

100 ml of water and 25 grams 30/50 fracturing sands were added into each of two glass bottles (200ml). 0.05 ml of Tegopren 6922, a di-quaternary polydimethylsiloxane from Degussa Corp., was added into one of the bottles. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow coal particulates settle down. The sands in the control bottle settled down immediately. In the bottle containing Tegopren 6922, sands settled down slower and a layer of sands was floating on the top and furthermore the sands were more fluid than those in the control one. The volume of settled sands in the one containing Tegopren 6922 was about twice of that in the control.

#### Example 11

A confidential and experimental hydraulic fracturing treatment was carried out in a gas well. The depth of the well was about 2500m and the formation temperature was about 76 °C. The fracturing fluid used was slick water, where a small amount of polymer was added into water to reduce friction pressure. Two proppants were used, one was 40/70 sands and the other was 30/50 sands. During the proppant stage, Tegopren-6922 was added into the fracturing fluid by continuous mixing at concentrations of 1 L/m<sup>3</sup> to 3 L/m<sup>3</sup> through the proppant stage, where the slurry was prepared and pumped into the formation through wellbore. Nitrogen gas was mixed with the fluid and the slurry during the operation. The samples taken during the operation showed that compared to sands in conventional slick water fracturing, the sands settled down slower and were more fluid.



As mentioned above, the present invention is particularly useful in many applications in the petroleum industry as well as in other industries. Examples include various well service operations including hydraulic fracturing, gravel pack, wellbore cleanout and drilling, particulate transportation through pipe lines, sand blasting, and excavation of a geological formation including tunneling, dredging, digging and the like.

When used in a hydraulic fracturing operation, a large amount of proppants can effectively be transported into a subterranean formation without using a viscosifier. It is not only cost-effective but also eliminates damage to the formation and proppant pack caused by polymer residues. An EHRC, for example, a di-quaternary polysiloxane can be mixed with an aqueous liquid and proppants on-the-fly to make the slurry and subsequently pumped into the formation during the proppant stage, either with or without a gas, or furthermore, a hydrocarbon surfactant, for example, a betaine surfactant, can be combined into the composition. It is particularly beneficial to use the slurry in so-called slick-water fracturing treatment. In conventional slick-water fracturing operations, due to the low viscosity of the fluid, only low concentrations of proppants can be effectively pumped deep into a formation, and moreover the proppants tend to settle down on the bottom of the fracture, resulting in lower conductivity. With the composition of the present invention, high concentration of proppants can easily be pumped deep into a formation and the proppants are more evenly distributed in the fracture, leading to improved conductivity of the proppant pack. Other aqueous fracturing fluids including water, brine, cross-linked polymer fluid and

viscoelastic surfactant fluid can also be employed in the present invention. An EHRC can be added straightly or premixed with a solvent or added as an emulsion during an operation. Similarly, one can use pre-hydrophobised proppants to make the slurries in the fracturing operations. Another benefit of the slurries of the present invention is that the aqueous liquid is re-useable after it is separated from the particulates. This has great significance considering there is limited water supply in a number of places.

The present invention also provides a new method for preventing proppant flowback after a fracturing treatment. In field operations, proppants can be pumped into a formation using the composition of the present invention. Alternatively, a fluid medium containing an EHRC can be pumped into the formation following the proppant stage to mix with particulates already in the formation. The particulates in the slurry tend to move cohesively in contrast to conventional slurries under the same conditions. It is worth noting that the cohesiveness among the proppant grains in the present slurry originates from hydrophobic interactions, instead of tackiness as described, for example in US Patent 6,047,772.

The slurry of the present invention is particularly useful in gravel-pack operations where sand slurry is normally pumped into a wellbore to prevent excessive amount of sands from flowing into the wellbore from the formation. The present method is cost effective and the sand pack formed has a high conductivity. Similarly, the slurry can also be used in so-called formation consolidation operations. In such an operation, a fluid containing an EHRC is

injected into a formation to increase cohesiveness among sand grains to consolidate the formation and to reduce sand production.

In drilling operations, an EHRC can be added into a water-based drilling fluid. It is particularly useful when the EHRC is added to water or brine for use as a drilling fluid. During a drilling operation, the fluid forms slurry in situ with cuttings and transports the cuttings out of the wellbore. A gas such as nitrogen or carbon dioxide can be mixed with the slurry during drilling. Since it is not necessary to use polymers or clays to viscosify the fluid, there is much less formation damage. Moreover, the cuttings can be easily removed on the surface and the aqueous liquid becomes re-useable. Different formations including sandstone, carbonate, shale and coal seams can be drilled using the slurry of the present invention.

Similarly in wellbore cleanout operations, for example, water containing an EHRC can circulate in the wellbore and form slurry with debris in situ. The debris is subsequently transported out of the wellbore as slurry. The fluid is re-useable after separation from the debris.

For transporting particulates through pipelines slurry can be prepared by mixing the ingredients and then pumping the slurry through the pipeline.



## CLAIMS:

1. An aqueous slurry composition, comprising
  - (a) an aqueous liquid;
  - (b) particulates; and
  - (c) a chemical compound for rendering the surface of the particulates extremely hydrophobic.
2. The aqueous slurry composition of claim 1 wherein the size of the particulates is in the range of 10-100 US mesh.
3. The aqueous slurry composition of claim 1 or 2 wherein the particulates are selected from a group consisting of sands, resin coated sands, ceramic, carbonate, bauxite, shale and coal particulates.
4. The composition of any one of claims 1 to 4, wherein the particulates are subterranean formation particulates.
5. The composition of any one of claims 1 to 4, wherein the chemical compound is selected from a group consisting of organosilanes, organosiloxanes, fluoro-organosilanes, fluoro-organosiloxanes and fluoro-organic compounds.
6. The composition of any one of claims 1 to 4, wherein the chemical compound is an organosilane having the formula



wherein R is an organic radical having 1-50 carbon atoms that may possess a functionality containing N, S, or P moieties that imparts desired characteristics, X is a halogen, alkoxy, acyloxy or amine and n has a value of 0-3.

7. The composition of any one of claims 1 to 4, wherein the chemical compound is selected from a group consisting of:

CH<sub>3</sub>SiCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>HSiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>HSiCl, CH<sub>3</sub>SiBr<sub>3</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)SiBr<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiBr<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SiBr<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiBr<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiBr, CH<sub>3</sub>HSiBr<sub>2</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>HSiBr, Si(OCH<sub>3</sub>)<sub>4</sub>, CH<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>,  
 CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>Si[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>,  
 C<sub>6</sub>H<sub>5</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>2</sub>=CH)Si(CH<sub>3</sub>)<sub>2</sub>Cl, (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>2</sub>, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>2</sub>=CH<sub>2</sub>)Si(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiOCH<sub>3</sub>, CH<sub>3</sub>HSi(OCH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>HSi(OCH<sub>3</sub>), CH<sub>3</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (CH<sub>2</sub>=CH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>Si(CH<sub>3</sub>COO)<sub>3</sub>, 3-aminotriethoxysilane,  
 methyldiethylchlorosilane, butyltrichlorosilane, diphenyldichlorosilane,  
 vinyltrichlorosilane, methyltrimethoxysilane, vinyltriethoxysilane,  
 vinyltris(methoxyethoxy)silane, methacryloxypropyltrimethoxysilane,  
 glycidoxypropyltrimethoxysilane, aminopropyltriethoxysilane, divinyl-di-2-  
 methoxysilane, ethyltributoxysilane, isobutyltrimethoxysilane,  
 hexyltrimethoxysilane, n-octyltriethoxysilane, dihexyldimethoxysilane,  
 octadecyltrichlorosilane, octadecyltrimethoxysilane,

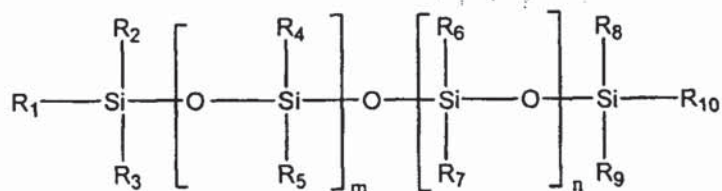
octadecyldimethylchlorosilane, octadecyldimethylmethoxysilane and quaternary ammonium silanes including 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride, 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium bromide, 3-(trimethylethoxysilylpropyl)didecylmethyl ammonium chloride, triethoxysilyl soyapropyl dimonium chloride, 3-(trimethylethoxysilylpropyl)didecylmethyl ammonium bromide, 3-(trimethylethoxysilylpropyl)didecylmethyl ammonium bromide, triethoxysilyl soyapropyl dimonium bromide,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_5)_3\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{CH}_3)_3\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_{13})_3\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_4\text{H}_9\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OHCl}^-$ ,  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{C}_2\text{H}_5)_3\text{Cl}^-$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ .

8. The composition of any one of claims 1 to 4, wherein the chemical compound is an organosiloxane.

9. The composition of claim 8, wherein the organosiloxane is selected from a group consisting of polyalkylsiloxanes, cationic polysiloxane, amphoteric polysiloxanes, sulfate polysiloxanes, phosphate polysiloxanes, carboxylate polysiloxanes, sulfonate polysiloxanes, thiosulfate polysiloxanes, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane.

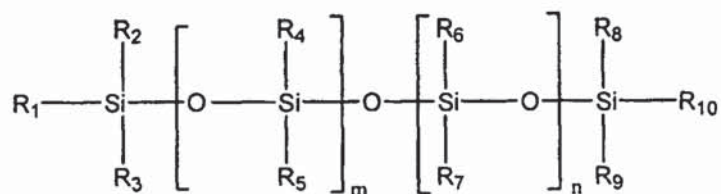


10. The composition of claim 8, wherein the organosiloxane is selected from a group consisting of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane.
11. The composition of claim 8, wherein the organosiloxane is a polyalkylsiloxane.
12. The composition of claim 8, wherein the organosiloxane is a cationic polysiloxane.
13. The composition of claim 8, wherein the organosiloxane is a quaternary polysiloxane.
14. The composition of claim 8, wherein the organosiloxane is an amphoteric polysiloxane.
15. The composition of claim 8, wherein the organosiloxane is a betaine polysiloxane.
16. The composition of claim 8 wherein the organosiloxane is selected from a group consisting of sulfate polysiloxane, sulfonate polysiloxane, phosphate polysiloxane, carboxylate polysiloxane and thiosulfate polysiloxane.
17. The composition of claim 8, wherein the organosiloxane is a cationic polysiloxane having the formula



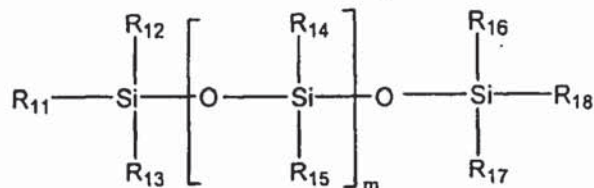
wherein each of R<sub>1</sub> to R<sub>6</sub> and R<sub>8</sub> to R<sub>10</sub>, represents alkyl containing 1-6 carbon atoms, typically a methyl group, R<sub>7</sub> represents a quaternary group and is associated with an anionic ion and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group, and m and n are from 1 to 200.

18. The composition of claim 8, wherein the organosiloxane is a betaine polysiloxane having the formula



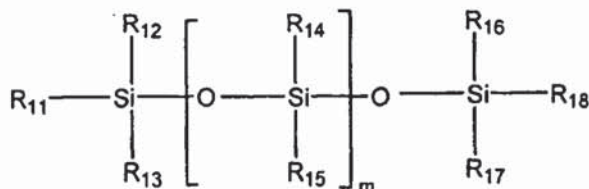
wherein each of  $R_1$  to  $R_6$  and  $R_8$  to  $R_{10}$ , represents alkyl containing 1-6 carbon atoms, typically a methyl group,  $R_7$  represents an organic betaine group and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group, and  $m$  and  $n$  are from 1 to 200.

19. The composition of claim 8, wherein the organosiloxane is according to the formula



where R<sub>12</sub> to R<sub>17</sub> each represents alkyl containing 1-6 carbon atoms, typically a methyl group, R<sub>11</sub> and R<sub>18</sub> each represents an organic betaine group and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group and m is 1 to 200.

20. The composition of claim 8, wherein the organosiloxane is according to the formula



where R<sub>12</sub> to R<sub>17</sub> each represents alkyl containing 1-6 carbon atoms, typically a methyl group, R<sub>11</sub> and R<sub>18</sub> each independently represents an organic quaternary group and is associated with an anionic ion and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group and m is 1 to 200.

21. The composition of any one of claims 1 to 20 further including a gas.
22. A fracturing fluid including the slurry composition according to any one of claims 1 to 21.
23. A gravel-pack fluid including the slurry composition according to any one of claims 1 to 21.
24. A drilling fluid including the slurry composition according to any one of claims 1 to 21.
25. The use of the slurry composition according to any one of claims 1 to 21 for transporting particulates through a pipeline.
26. The use of the slurry composition according to any one of claims 1 to 21 in a well service operation.
27. A method of making an aqueous slurry composition comprising the steps



(a) treating particulates with a chemical compound to render the particulate surface extremely hydrophobic, and then

(b) mixing the treated particulates with an aqueous liquid to make an aqueous slurry.

28. A method for making an aqueous slurry composition comprising steps of mixing

(a) an aqueous liquid;

(b) particulates; and

(c) a chemical compound for rendering the surface of the particulates extremely hydrophobic.

29. The method of claim 27 or 28 wherein the size of particulates is in the range of 10–100 US mesh.

30. The method of any one of claims 27 to 29 wherein the particulates are selected from a group consisting of sands, resin coated sands, ceramic, carbonate, bauxite, shale and coal particulates.

31. The method of any one of claims 27 to 30, further including the step of mixing the slurry with a gas.

32. The method of any one of claims 27 to 31 wherein the chemical compound is selected from a group consisting of organosilanes, organosiloxanes, fluoro-organosilanes, fluoro-organosiloxanes and fluoro-organic compounds.

33. The method of any one of claims 27 to 31 wherein the chemical compound is an organosilane having the formula



wherein R is an organic radical having 1-50 carbon atoms that may possess a functionality containing N, S, or P moieties that imparts desired characteristics, X is a halogen, alkoxy, acyloxy or amine and n has a value of 0-3.

34. The method of any one of claims 27 to 31 wherein the chemical compound in claim 21 is an organosiloxane selected from a group consisting of polyalkylsiloxanes, cationic polysiloxane, amphoteric polysiloxanes, sulfate polysiloxanes, phosphate polysiloxanes, carboxylate polysiloxanes, sulfonate polysiloxanes, thiosulfate polysiloxanes, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane.
35. The method of any one of claims 27 to 31 wherein the chemical compound is a polyalkylsiloxane.
36. The method of any one of claims 27 to 31 wherein the chemical compound is a cationic polysiloxane.
37. The method of any one of claims 27 to 31 wherein the chemical compound is a quaternary polysiloxane.
38. The method of any one of claims 27 to 31 wherein the chemical compound is an amphoteric polysiloxane.
39. The method of any one of claims 27 to 31 wherein the chemical compound is a betaine polysiloxane.

40. The method of any one of claims 27 to 31 wherein the chemical compound is selected from a group consisting of sulfate polysiloxane, sulfonate polysiloxane, phosphate polysiloxane, carboxylate polysiloxane and thiosulfate polysiloxane.
41. The method of any one of claims 27 to 40 further including the step of mixing a surfactant with the slurry composition.
42. The slurry composition of any one of claims 1 to 21 further including a surfactant.
43. The fracturing fluid of claim 22 further including a surfactant.
44. The gravel-pack fluid of claim 23 further including a surfactant.
45. The drilling fluid of claim 24 further including a surfactant.
46. A wellbore cleanout fluid including the slurry composition according to any one of claims 1 to 21.



(12)

(21) 2 509 115

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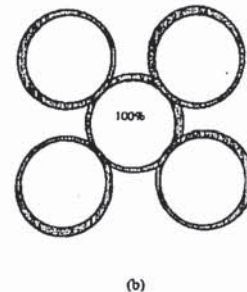
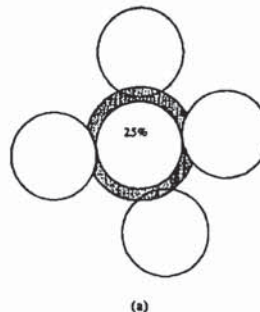
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(54) METHODES DE REVETEMENT DE RESINE ET DE MELANGE D'AGENT DE SOUTENEMENT ENDUIT DE RESINE

(54) METHODS OF COATING RESIN AND BLENDING RESIN-COATED PROPPANT

(57)

A method of consolidating particulates comprising providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin or tackifying agent and wherein the second portion of particulates is substantially free of resin or tackifying agent; introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates to form a particulate pack in the portion of the subterranean formation; and, allowing the resin to substantially consolidate the particulate pack. A particulate slurry for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin or tackifying agent and wherein the second portion of particulates is substantially free of resin or tackifying agent.





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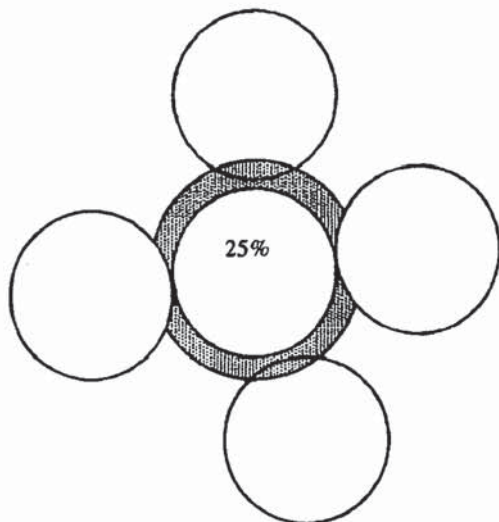
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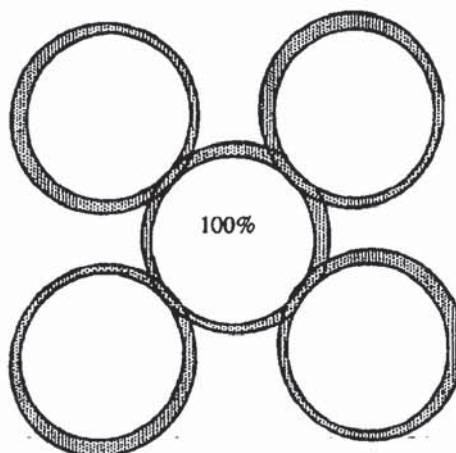
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(a)



(b)

(57) Abrégé/Abstract:

A method of consolidating particulates comprising providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin or tackifying agent and wherein the second portion of particulates is substantially free of resin or tackifying agent; introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates to form a particulate pack in the portion of the subterranean formation; and, allowing the resin to substantially consolidate the particulate pack. A particulate slurry for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin or tackifying agent and wherein the second portion of particulates is substantially free of resin or tackifying agent.

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**METHODS OF COATING RESIN AND BLENDING RESIN-COATED PROPPANT****ABSTRACT**

A method of consolidating particulates comprising providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin or tackifying agent and wherein the second portion of particulates is substantially free of resin or tackifying agent; introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates to form a particulate pack in the portion of the subterranean formation; and, allowing the resin to substantially consolidate the particulate pack. A particulate slurry for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin or tackifying agent and wherein the second portion of particulates is substantially free of resin or tackifying agent.



## METHODS OF COATING RESIN AND BLENDING RESIN-COATED PROPPANT

### BACKGROUND

The present invention relates to methods and compositions for consolidating particulates in subterranean formations. More particularly, the present invention relates to methods of coating particulates with consolidating agents and blending consolidating agent-coated particulates.

Subterranean operations often use particulates coated with consolidating agents such as tackifying agents and/or resins. One example of a production stimulation operation using coated particulates is hydraulic fracturing, wherein a formation is treated to increase its permeability by hydraulically fracturing the formation to create or enhance one or more cracks or "fractures." In most cases, a hydraulic fracturing treatment involves pumping a proppant-free, viscous fluid (known as a pad fluid) into a subterranean formation faster than the fluid can escape into the formation so that the pressure in the formation rises and the formation breaks, creating an artificial fracture or enlarging a natural fracture. Then a proppant is generally added to the fluid to form a slurry that is pumped into the fracture to prevent the fracture from closing when the pumping pressure is released. A portion of the proppant may be coated with a tackifying agent, *inter alia*, to prevent fines from migrating into the proppant pack. A portion of the proppant may also be coated with curable resin so that, once cured, the placed proppant forms a consolidated mass and prevents the proppant from flowing back during production of the well.

An example of a well completion operation using a treating fluid containing coated particulates is gravel packing. Gravel packing treatments are used, *inter alia*, to reduce the migration of unconsolidated formation particulates into the well bore. In gravel packing operations, particles known in the art as gravel are carried to a well bore by a hydrocarbon or water carrier fluid. That is, the particulates are suspended in a carrier fluid, which may be viscosified, and the carrier fluid is pumped into a well bore in which the gravel pack is to be placed. The carrier fluid leaks off into the subterranean zone and/or is returned to the surface while the particulates are left in the zone. The resultant gravel pack acts as a filter to separate formation sands from produced fluids while permitting the produced fluids to flow into the well bore. A portion of the gravel may be coated with resin or tackifying agent, *inter alia*, to further help control the migration of formation fines. Typically, gravel pack operations involve placing a gravel pack screen in the well bore and packing the surrounding annulus

between the screen and the well bore with gravel designed to prevent the passage of formation sands through the pack. The gravel pack screen is generally a type of filter assembly used to support and retain the gravel placed during the gravel pack operation. A wide range of sizes and screen configurations are available to suit the characteristics of a particular well bore, the production fluid, and the subterranean formation sands. When installing the gravel pack, the gravel is carried to the formation in the form of a slurry by mixing the gravel with a viscosified carrier fluid. Once the gravel is placed in the well bore, the viscosity of the carrier fluid is reduced, and it is returned to the surface. Such gravel packs may be used to stabilize the formation while causing minimal impairment to well productivity. The gravel, *inter alia*, acts to prevent formation sands from occluding the screen or migrating with the produced fluids, and the screen, *inter alia*, acts to prevent the gravel from entering the well bore.

In some situations the processes of hydraulic fracturing and gravel packing are combined into a single treatment to provide stimulated production and an annular gravel pack to reduce formation sand production. Such treatments are often referred to as "frac pack" operations. In some cases, the treatments are completed with a gravel pack screen assembly in place, and the hydraulic fracturing treatment being pumped through the annular space between the casing and screen. In such a situation, the hydraulic fracturing treatment usually ends in a screen out condition creating an annular gravel pack between the screen and casing. This allows both the hydraulic fracturing treatment and gravel pack to be placed in a single operation.

### SUMMARY OF THE INVENTION

The present invention relates to methods and compositions for consolidating particulates in subterranean formations. More particularly, the present invention relates to methods of coating particulates with consolidating agents and blending consolidating agent-coated particulates.

Some embodiments of the present invention provide methods of consolidating particulates comprising providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin and wherein the second portion of particulates is substantially free of resin; introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates form a particulate pack in the



portion of the subterranean formation; and, allowing the resin to substantially consolidate the particulate pack.

Other embodiments of the present invention provide methods of consolidating particulates comprising providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with tackifying agent and wherein the second portion of particulates is substantially free of tackifying agent; introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates form a particulate pack in the portion of the subterranean formation; and, allowing the tackifying agent to substantially consolidate the particulate pack.

Other embodiments of the present invention provide particulate slurries for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin and wherein the second portion of particulates is substantially free of resin.

Other embodiments of the present invention provide particulate slurries for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with tackifying agent and wherein the second portion of particulates is substantially free of tackifying agent.

The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 illustrates a stylized view of the distinction between a traditional resin coating (b) and the resin coatings of the present invention (a).

### **DESCRIPTION OF PREFERRED EMBODIMENTS**

The present invention relates to methods and compositions for consolidating particulates in subterranean formations. More particularly, the present invention relates to methods of coating particulates with consolidating agents and blending consolidating agent-coated particulates.

While it has been previously believed that in order to achieve strong, solid, conductive particulate packs it was necessary to coat as great a percentage of the particulates as possible, we have found that it is actually more beneficial to coat only a portion of the



particulates, but to coat more heavily that portion with a relatively larger weight percentage of consolidating agent than has been previously used. By using a substantially homogeneous mixture of relatively heavily coated particulates and uncoated particulates to create a particulate pack, particular embodiments of the methods of the present invention offer economical approaches to coating particulates with resin while maintaining or enhancing the consolidation strength of the particulate pack.

In particular embodiments of the present invention, a first portion of particulates, typically ranging from about 10% to about 60% by weight of the total amount of particulates, is coated with a consolidating agent; then the consolidating agent-coated first portion of particulates is combined with a servicing fluid (such as a fracturing fluid or gravel packing fluid) with the remainder of the (uncoated) particulates (90% to 40% uncoated, depending on the percentage of consolidating agent-coated proppant). The mixing of the consolidating agent-coated and uncoated particulates in the servicing fluid allows the coated particulates to be distributed among the uncoated particulates. In certain embodiments, the resin consolidating agent-coated and uncoated particulates are substantially uniformly intermingled in the servicing fluid. When introduced into a subterranean fracture, the mixture of coated and uncoated particulates cures to form a particulate pack that may exhibit a consolidation strength equivalent to, and often even higher than, a traditional particulate pack comprised entirely of coated particulates.

Contributing to this enhanced consolidation strength is the fact that particular embodiments of the present invention use coated particulates that feature a thicker coating of consolidating agent than those found in traditional subterranean applications. For example, in traditional applications, consolidating agent-coated particulates are normally coated with a consolidating agent in an amount in the range of 3% to 5% by weight of the particulates. However, in particular embodiments of the present invention, the particulates used may be coated with a consolidating agent in an amount of at least about 5%, or in the range of from about 5.5% to about 50% by weight of the particulates. In other embodiments, the particulates used may be coated with a consolidating agent in an amount of at least about 7%. In other embodiments, the particulates used may be coated with a consolidating agent in an amount of at least about 10%. In other embodiments, the particulates used may be coated with a consolidating agent in an amount of at least about 15%. In accordance with certain methods of the present invention, one method of achieving such greater coatings of

consolidating agent without greatly increasing costs is to use the same amount of consolidating agent that would be used to coat an entire batch of particulates in a traditional subterranean application, but use that amount of consolidating agent to coat only a fraction of the total amount of particulates.

The greater coating of consolidating agent on the first (coated) portion of the particulates may have numerous benefits. By coating only a portion of the particulates with this greater coating, more consolidating agent is concentrated at the contact points between the grains of particulates. This may allow the consolidating agent to build stronger grain-to-grain adhesions. Additionally, it is believed that the thicker coating of consolidating agent on the particulate may help to create larger interstitial spaces between the individual particulates. These larger interstitial spaces, or voids, may help enhance the conductivity of the particulate packs without reducing their consolidation strength. A stylized view of the distinction between the traditional consolidating agent coating and the consolidating agent coatings of the present invention is provided in Figure 1. Figure 1(a) illustrates a situation wherein only about 20-25% of the particulates is coated with consolidating agent, but that percentage is coated with a relatively greater coating of consolidating agent. Figure 1(b) illustrates a situation wherein about 90-100% of the particulates are coated with a traditional thickness coating of consolidating agent. In Figures 1(a) and 1(b), the same amount of consolidating agent has been used to coat, but in Figure 1(a) all of the consolidating agent is on one particulate while in Figure 1(b) the resin is spread among five particulates.

The methods of the present invention may be used, *inter alia*, such that the total volume of consolidating agent used is less than that traditionally needed to effect good consolidation, thus resulting in a direct cost decrease due to the use of less consolidating agent. Alternatively, as described above, the methods of the present invention may use the same amount of consolidating agent coated on a smaller portion of the particulates, in that case while a direct cost benefit of reduced consolidating agent usage may not be seen, cost savings may still occur due to the fact that coating fewer particulates may result in simplified operating procedures, reduced horsepower requirement, and reduced equipment usage. It is within the ability of one skilled in the art to determine the minimum level of consolidation needed for a job and to select the level of consolidating agent accordingly. For example, when using curable resins, consolidation strengths (when considered in terms term of



unconfined compressive strengths, UCC) may range from about 20 psi to 2,000 psi, depending on the resin concentration, cure time, and cure temperature.

Particulates used in accordance with the present invention are generally of a size such that formation sands that may migrate with produced fluids are prevented from being produced from the subterranean zone. Any suitable proppant or gravel may be used, including, but not limited to, graded sand, bauxite, ceramic materials, glass materials, walnut hulls, nut shells, polymer beads, and the like. Generally, the particulates have a size in the range of from about 4 to about 400 mesh, U.S. Sieve Series. In some embodiments of the present invention, the particulates are graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series.

As mentioned above, in accordance with the preferred methods of the present invention, only a portion of the total amount of proppant is coated with consolidating agent. In certain particular embodiments of the present invention, the particulates may be purchased as pre-coated from a commercial supplier (RCP). Suitable commercially available RCP materials include, but are not limited to, pre-cured resin-coated sand, curable resin-coated sand, curable resin-coated ceramics, single-coat, dual-coat, or multi-coat resin-coated sand, ceramic, or bauxite. Some examples available from Borden Chemical, Columbus, Ohio, are "XRT<sup>TM</sup> CERAMAX P," "CERAMAX I," "CERAMAX P," "ACFRAC BLACK," "ACFRAC CR," "ACFRAC SBC," "ACFRAC SC," and "ACFRAC LTC." Some examples available from Santrol, Fresno, Texas, are "HYPERPROP G2," "DYNAPROP G2," "MAGNAPROP G2," "OPTIPROP G2," "SUPER HS," "SUPER DC," "SUPER LC," and "SUPER HT." Typically, these products come from the supplier with a coating of resin in an amount in the range of about 3% to about 5% by weight of the proppant. However, as mentioned above, embodiments of the present invention generally employ a greater coating of than traditional RCP materials may be coated with consolidating agent in an amount of at least about 5%, or in the range of from about 5.5% to about 50% by weight of the particulates. In other embodiments, the particulates used may be coated with a consolidating agent in an amount of at least about 7%. In other embodiments, the particulates used may be coated with a consolidating agent in an amount of at least about 10%. In other embodiments, the particulates used may be coated with a consolidating agent in an amount of at least about 15%.



One suitable type of consolidating agent is a resin. Suitable resin compositions include those resins that are capable of forming a hardened, consolidated mass. Suitable resins include, but are not limited to, two-component epoxy-based resins, novolak resins, polyepoxide resins, phenol-aldehyde resins, urea-aldehyde resins, urethane resins, phenolic resins, furan/furfuryl alcohol resins, phenolic/latex resins, phenol formaldehyde resins, polyester resins and hybrids and copolymers thereof, polyurethane resins and hybrids and copolymers thereof, acrylate resins, and mixtures thereof. Some suitable resins, such as epoxy resins, may be of the two-component variety mentioned above and use an external catalyst or activator. Other suitable resins, such as furan resins generally require a time-delayed catalyst or an external catalyst to help activate the polymerization of the resins if the cure temperature is low (*i.e.*, less than 250°F), but will cure under the effect of time and temperature if the formation temperature is above about 250°F, preferably above about 300°F. Selection of a suitable resin coating material may be affected by the temperature of the subterranean formation to which the fluid will be introduced. By way of example, for subterranean formations having a bottom hole static temperature ("BHST") ranging from about 60°F to about 250°F, two-component epoxy-based resins comprising a hardenable resin component and a hardening agent component containing specific hardening agents may be preferred. For subterranean formations having a BHST ranging from about 300°F to about 600°F, a furan-based resin may be preferred. For subterranean formations having a BHST ranging from about 200°F to about 400°F, either a phenolic-based resin or a one-component HT epoxy-based resin may be suitable. For subterranean formations having a BHST of at least about 175°F, a phenol/phenol formaldehyde/furfuryl alcohol resin also may be suitable. It is within the ability of one skilled in the art, with the benefit of this disclosure, to select a suitable resin for use in embodiments of the present invention and to determine whether a catalyst is required to trigger curing.

As mentioned above, particular embodiments of the present invention may employ an activator, or external catalyst, to trigger the curing of certain resin compositions, for example, two-component epoxy resins. In an exemplary embodiment, such an activator may be delivered by at least partially coating the non-resin-coated portion of the particulates with the activator prior to mixing the two portions of particulates together. Once mixed with the resin-coated particulates, the activator may trigger the curing of the resin, facilitating the consolidation of the particulates. When applied to the non-resin-coated portion of the

particulates, the activator is typically present in an amount in the range of from about 0.01% to about 25% by weight of the particulates. Activators suitable for use in accordance with the present invention may depend on the resin employed in a particular embodiment. Examples of suitable activators include an alcohol; a ketone; an ester; an ether; an amide; benzene sulfonic acid; sulfuric acid; methane sulfonic acid; trichloroacetic acid; hydrochloric acid; hydrofluoric acid; ferric chloride; toluene sulfonic acid; chlorobenzene sulfonic acid; nitric acid; perchloric acid; a water soluble multivalent metal salt catalyst comprising at least one multivalent ion of either manganese, zinc, cadmium, magnesium, cobalt, nickel, copper, tin, iron, lead, or calcium; and combinations thereof. With the benefit of this disclosure, it is within the ability of one skilled in the art to select an activator appropriate for use with a selected resin, should an activator be necessary, and the amount necessary to trigger curing.

Similarly, particular embodiments of the present invention may also employ a curing agent to facilitate the curing of the resin. In an exemplary embodiment, such a curing agent may be delivered by at least partially coating the non-resin-coated portion of the particulates with the curing agent prior to mixing the two portions of particulates together. Once mixed with the coated particulates, the curing agent may facilitate the curing of the resin, and therefore the consolidation of the particulates. When applied to the non-resin-coated portion of the particulates, the curing agent is typically present in an amount in the range of from about 0.01% to about 25% by weight of the particulates. Curing agents suitable for use in accordance with the present invention may depend on the resin employed in a particular embodiment. Examples of suitable curing agents include amines, polyamines, amides, polyamides, hexachloroacetone, 1,1,3-trichlorotrifluoroacetone, benzotrichloride, benzylchloride, benzalchloride, 4,4'-diaminodiphenyl sulfone, and combinations thereof. With the benefit of this disclosure, it is within the ability of one skilled in the art to select a curing agent appropriate for use with a selected resin, should a curing agent be necessary, and the amount necessary to trigger curing.

In particular embodiments of the present invention, the consolidating agent may be a tackifying agent. In other embodiments, the consolidating agent may be a combination of resin and tackifying agent. When used in conjunction with resin coated particulates, a tackifying agent is typically applied after the application of the resin in an amount of from about 2% to about 10% by weight of the particulates. When used in place of a resin, the



tackifying agent is typically present in an amount of from about 5% to about 25% by weight of the particulates.

Compositions suitable for use as tackifying agents in accordance with the present invention comprise any compound that, when in liquid form or in a solvent solution, will form a non-hardening coating upon a particulate. In particular embodiments, tackifying agents may include polyamides that are liquids or in solution at the temperature of the subterranean formation such that they are, by themselves, non-hardening when introduced into the subterranean formation. One such compound is a condensation reaction product comprised of commercially available polyacids and a polyamine. Such commercial products include compounds such as mixtures of C<sub>36</sub> dibasic acids containing some trimer and higher oligomers and also small amounts of monomer acids produced from fatty acids, maleic anhydride, and acrylic acid, and the like. Such acid compounds are commercially available from companies such as Witco Corporation, Union Carbide, Chemtall, and Emery Industries. The reaction products are available from, for example, Champion Technologies, Inc., and Witco Corporation. Additional compounds that may be used as tackifying agents include liquids and solutions of, for example, polyesters, polycarbonates and polycarbamates, natural resins such as shellac, and the like. Suitable tackifying agents are described in U.S. Patent Number 5,853,048 issued to Weaver, *et al.*, and U.S. Patent Number 5,833,000 issued to Weaver, *et al.*, the relevant disclosures of which are herein incorporated by reference.

Tackifying agents suitable for use in the present invention may be either used such that they form non-hardening coating or they may be combined with a multifunctional material capable of reacting with the tackifying compound to form a hardened coating. A "hardened coating" as used herein means that the reaction of the tackifying compound with the multifunctional material will result in a substantially non-flowable reaction product that exhibits a higher compressive strength in a consolidated agglomerate than the tackifying compound alone with the particulates. In this instance, the tackifying agent may function similarly to a hardenable resin. Multifunctional materials suitable for use in the present invention include, but are not limited to, aldehydes such as formaldehyde, dialdehydes such as glutaraldehyde, hemiacetals or aldehyde-releasing compounds, diacid halides, dihalides such as dichlorides and dibromides, polyacid anhydrides such as citric acid, epoxides, furfuraldehyde, glutaraldehyde or aldehyde condensates and the like, and combinations thereof. In some embodiments of the present invention, the multifunctional material may be



mixed with the tackifying compound in an amount of from about 0.01% to about 50% by weight of the tackifying compound to effect formation of the reaction product. In some preferable embodiments, the compound is present in an amount of from about 0.5% to about 1% by weight of the tackifying compound. Suitable multifunctional materials are described in U.S. Patent Number 5,839,510 issued to Weaver, *et al.*, the relevant disclosure of which is herein incorporated by reference.

The tackifying agent may act, *inter alia*, to enhance the grain-grain contact between individual particulates. Moreover, the tackifying agent may soften any previously-applied, partially cured resin on the particulates. This dual action of the tackifying agent may improve the final consolidation strength of a particulate pack made in accordance with the present invention.

Any servicing fluid suitable for a subterranean application may be used in accordance with the teachings of the present invention, including aqueous gels, emulsions, and other suitable fracturing fluids. Suitable aqueous gels are generally comprised of water and one or more gelling agents. Suitable emulsions may be invert or regular and may be comprised of two immiscible liquids such as an aqueous gelled liquid and a liquefied, normally gaseous fluid, such as nitrogen. In certain exemplary embodiments of the present invention, the servicing fluids are aqueous gels comprised of water, a gelling agent for gelling the water and increasing its viscosity, and, optionally, a cross-linking agent for cross-linking the gel and further increasing the viscosity of the fluid. The increased viscosity of the gelled, or gelled and cross-linked, fracturing fluid, *inter alia*, reduces fluid loss and allows the fracturing fluid to transport significant quantities of suspended proppant particles.

To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should the following examples be read to limit or define the scope of the invention.

## EXAMPLES

### Example 1

Four 250-gram samples of 20/40-mesh size bauxite proppant were coated with a total of 7.8 cc of high-temperature epoxy resin. The samples were coated such that in each sample a different portion of the sample was coated with the resin (*e.g.*, 100%, 75%, 50%, and 25%). Each resin-coated proppant sample was then poured into a cross-linking gel carrier fluid while the fluid was stirred at high speed using an overhead stirrer. After 10 seconds of high

speed stirring, the proppant slurries were stirred at very low speed to stimulate the effect of pumping and suspending the proppant slurries in fractures during hydraulic fracturing treatments. Each proppant slurry was then poured into a brass chamber, packed, and cured at 325 °F for 20 hours. After curing, the consolidated cores were obtained, cut into size, and unconfined compressive strengths were determined for each sample composition. These unconfined compressive strengths are shown in Table 1, in which:

- sample composition No. 1 contains 250 grams of proppant coated with a total of 7.8 cc of resin;
- sample composition No. 2 contains 250 grams of proppant, 188 grams of which were coated with a total of 7.8 cc of resin;
- sample composition No. 3 contains 250 grams of proppant, 125 grams of which were coated with a total of 7.8 cc of resin; and
- sample composition No. 4 contains 250 grams of proppant, 62 grams of which were coated with a total of 7.8 cc of resin.

TABLE 1

Proppant	Unconfined Compressive Strength (psi)
Sample Composition No. 1	480
Sample Composition No. 2	565
Sample Composition No. 3	580
Sample Composition No. 4	545

From Table 1, it is evident that the unconfined compressive strengths of the sample compositions were higher when only a portion of the sample had been coated with resin.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.



What is claimed is:

1. A method of consolidating particulates comprising:  
providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin and wherein the second portion of particulates is substantially free of resin;  
introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates form a particulate pack in the portion of the subterranean formation; and,  
allowing the resin to substantially consolidate the particulate pack.
2. The method of claim 1, wherein the portion of a subterranean formation comprises a portion of a fracture or a portion of the annulus surrounding a well bore.
3. The method of claim 1, wherein the resin comprises at least one component chosen from an epoxy-based resin, a novolak resin, a polyepoxide resin, a phenol-aldehyde resin, a urea-aldehyde resin, a urethane resin, a phenolic resin, a furan/furfuryl alcohol resin, a phenolic/latex resin, a phenol formaldehyde resin, a polyester resin, a polyurethane resin, an acrylate resin, and a combination thereof.
4. The method of claim 1, wherein the first portion of particulates comprises between about 10% and about 60%, by weight of the combined weight of the first and second portions of particulates.
5. The method of claim 1, wherein the resin is present in an amount in the range of from about 5% to about 50% by weight of the first portion of particulates.
6. The method of claim 1, wherein the resin comprises a curable resin.
7. The method of claim 1, wherein the resin comprises a non-curable resin.
8. The method of claim 1, wherein the first portion of particulates is at least partially coated with a tackifying agent.
9. The method of claim 8, wherein the tackifying agent is present in an amount in the range of from about 2% to about 7% by weight of the first portion of particulates.



10. The method of claim 8, wherein the tackifying agent comprises at least one component chosen from a polyamide, a polyester, a polycarbonate, a polycarbamate, a natural resin, and a combination thereof.

11. The method of claim 8, wherein the first portion of the particulates is at least partially coated with a multifunctional material.

12. The method of claim 11, wherein the multifunctional material comprises at least one component chosen from an aldehyde, a hemiacetal, an aldehyde-releasing compound, a diacid halide, a dihalide, a polyacid anhydride, an epoxide, a furfuraldehyde, a glutaraldehyde, an aldehyde condensate, and a combination thereof.

13. The method of claim 11, wherein the multifunctional material is present in an amount in the range of from about 0.01% to about 50% by weight of the tackifying agent.

14. The method of claim 11, wherein the multifunctional material is present in an amount in the range of from about 0.1% to about 1% by weight of the tackifying agent.

15. The method of claim 1, wherein the second portion of particulates is at least partially coated with an activator.

16. The method of claim 15, wherein the activator is present in an amount in the range of from about 0.01% to about 25% by weight of the second portion of particulates.

17. The method of claim 15, wherein the activator comprises at least one component chosen from an alcohol; a ketone; an ester; an ether; an amide; benzene sulfonic acid; sulfuric acid; methane sulfonic acid; trichloroacetic acid; hydrochloric acid; hydrofluoric acid; ferric chloride; toluene sulfonic acid; chlorobenzene sulfonic acid; nitric acid; perchloric acid; a water soluble multivalent metal salt catalyst comprising at least one multivalent ion of either manganese, zinc, cadmium, magnesium, cobalt, nickel, copper, tin, iron, lead, or calcium; and a combination thereof.

18. The method of claim 1, wherein the second portion of particulates is at least partially coated with a curing agent.

19. The method of claim 18, wherein the curing agent is present in an amount in the range of from about 0.01% to about 25% by weight of the second portion of particulates.

20. The method of claim 18, wherein the curing agent comprises at least one component chosen from an amine, a polyamine, an amide, a polyamide, hexachloroacetone, 1,1,3-trichlorotrifluoroacetone, benzotrichloride, benzylchloride, benzalchloride, 4,4'-diaminodiphenyl sulfone, and a combination thereof.

21. A method of consolidating particulates comprising:  
providing a slurry comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with tackifying agent and wherein the second portion of particulates is substantially free of tackifying agent;

introducing the slurry into a portion of a subterranean formation such that the first portion of particulates and second portion of particulates form a particulate pack in the portion of the subterranean formation; and,

allowing the tackifying agent to substantially consolidate the particulate pack.

22. The method of claim 21, wherein the portion of a subterranean formation comprises a portion of a fracture or a portion of the annulus surrounding a well bore.

23. The method of claim 21, wherein the first portion of particulates comprises between about 10% and about 60%, by weight, of the combined weight of the first and second portions of particulates.

24. The method of claim 21, wherein the tackifying agent is present in an amount in the range of about 5% to about 10% by weight of the first portion of particulates.

25. The method of claim 21, wherein the tackifying agent comprises at least one component chosen from a polyamide, polyester, polycarbonate, polycarbamate, a natural resin, and a combination thereof.

26. The method of claim 21, wherein the first portion of particulates is at least partially coated with a multifunctional material.

27. The method of claim 26, wherein the multifunctional material comprises at least one component chosen from an aldehyde, a hemiacetal, an aldehyde-releasing compound, a diacid halide, a dihalide, a polyacid anhydride, an epoxide, a furfuraldehyde, a glutaraldehyde, an aldehyde condensate, and a combination thereof



28. The method of claim 26, wherein the multifunctional material is present in an amount in the range of from about 0.01% to about 50% by weight of the tackifying agent.

29. The method of claim 26, wherein the multifunctional material is present in an amount in the range of from about 0.1% to about 1% by weight of the tackifying agent.

30. A particulate slurry for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with resin and wherein the second portion of particulates is substantially free of resin.

31. The particulate slurry of claim 30, wherein the resin comprises at least one component chosen from an epoxy-based resin, a novolak resin, a polycycloheximide resin, a phenol-aldehyde resin, a urea-aldehyde resin, a urethane resin, a phenolic resin, a furan/furfuryl alcohol resin, a phenolic/latex resin, a phenol formaldehyde resin, a polyester resin, a polyurethane resin, an acrylate resin, and a combination thereof.

32. The particulate slurry of claim 30, wherein the first portion of particulates comprises between about 10% and about 60%, by weight of the combined weight of the first and second portions of particulates.

33. The particulate slurry of claim 30, wherein the resin is present in an amount in the range of about 5% to about 50% by weight of the first portion of particulates.

34. The particulate slurry of claim 30, wherein the resin comprises a curable resin.

35. The particulate slurry of claim 30, wherein the resin comprises a non-curable resin.

36. The particulate slurry of claim 30, wherein the first portion of particulates is at least partially coated with a tackifying agent.

37. The particulate slurry of claim 36, wherein the tackifying agent is present in an amount in the range of from about 2% to about 7% by weight of the first portion of particulates.

38. The particulate slurry of claim 36, wherein the tackifying agent comprises at least one component chosen from a polyamide, polyester, polycarbonate, polycarbamate, a natural resin, and a combination thereof.



39. The particulate slurry of claim 36, wherein the particulate slurry further comprises a multifunctional material.

40. The particulate slurry of claim 39, wherein the multifunctional material comprises at least one component chosen from an aldehyde, a hemiacetal, an aldehyde-releasing compound, a diacid halide, a dihalide, a polyacid anhydride, an epoxide, a furfuraldehyde, a glutaraldehyde, an aldehyde condensate, and a combination thereof.

41. The particulate slurry of claim 39, wherein the multifunctional material is present in an amount in the range of from about 0.01% to about 50% by weight of the tackifying agent.

42. The particulate slurry of claim 39, wherein the multifunctional material is present in an amount in the range of from about 0.1% to about 1% by weight of the tackifying agent.

43. The particulate slurry of claim 30, wherein the second portion of particulates is at least partially coated with an activator.

44. The particulate slurry of claim 43, wherein the activator is present in an amount in the range of from about 0.01% to about 25% by weight of the second portion of particulates.

45. The particulate slurry of claim 43, wherein the activator comprises at least one component chosen from an alcohol; a ketone; an ester; an ether; an amide; benzene sulfonic acid; sulfuric acid; methane sulfonic acid; trichloroacetic acid; hydrochloric acid; hydrofluoric acid; ferric chloride; toluene sulfonic acid; chlorobenzene sulfonic acid; nitric acid; perchloric acid; a water soluble multivalent metal salt catalyst comprising at least one multivalent ion of either manganese, zinc, cadmium, magnesium, cobalt, nickel, copper, tin, iron, lead, or calcium; and a combination thereof.

46. The particulate slurry of claim 30, wherein the second portion of particulates is at least partially coated with a curing agent.

47. The particulate slurry of claim 46, wherein the curing agent is present in an amount in the range of from about 0.01% to about 25% by weight of the second portion of particulates.

48. The particulate slurry of claim 46, wherein the curing agent comprises at least one component chosen from an amine, a polyamine, an amide, a polyamide,

hexachloroacetone, 1,1,3-trichlorotrifluoroacetone, benzotrichloride, benzylchloride, benzalchloride, 4,4'-diaminodiphenyl sulfone, and a combination thereof.

49. A particulate slurry for use in subterranean formations comprising a carrier fluid, a first portion of particulates, and a second portion of particulates wherein the first portion of particulates is at least partially coated with tackifying agent and wherein the second portion of particulates is substantially free of tackifying agent.

50. The particulate slurry of claim 49, wherein the first portion of particulates comprises between about 10% and about 60%, by weight of the combined weight of the first and second portions of particulates.

51. The particulate slurry of claim 49, wherein the tackifying agent is present in an amount in the range of about 5% to about 10% by weight of the first portion of particulates.

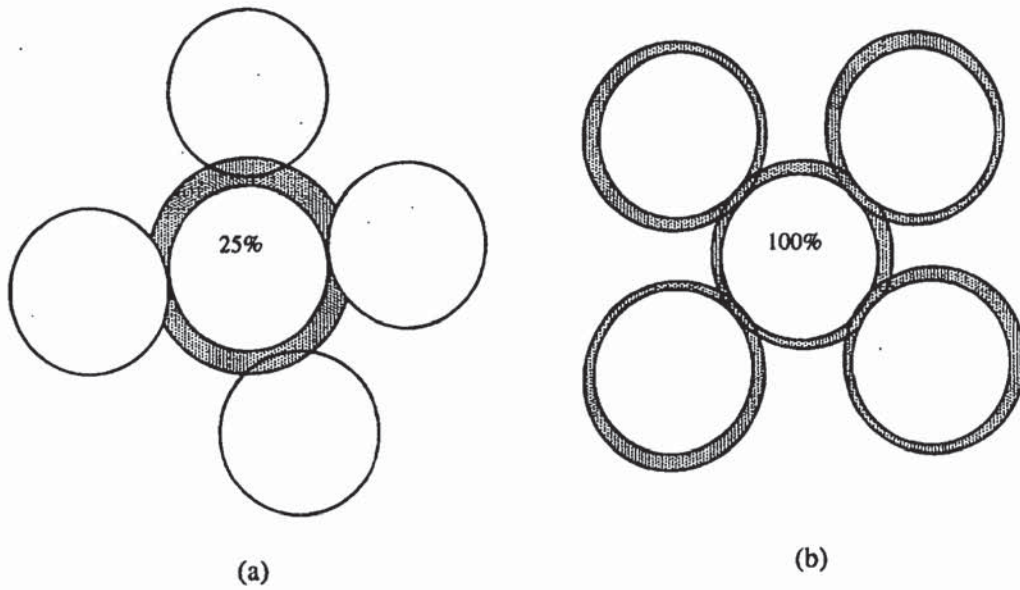
52. The particulate slurry of claim 49, wherein the tackifying agent comprises at least one component chosen from a polyamide, a polyester, a polycarbonate, a polycarbamate, a natural resin, and a combination thereof.

53. The particulate slurry of claim 49, wherein the proppant slurry further comprises a multifunctional material.

54. The particulate slurry of claim 53, wherein the multifunctional-material comprises at least one component chosen from an aldehyde, a hemiacetal, an aldehyde-releasing compound, a diacid halide, a dihalide, a polyacid anhydride, an epoxide, a furfuraldehyde, a glutaraldehyde, an aldehyde condensate, and a combination thereof.

55. The particulate slurry of claim 53, wherein the multifunctional-material is present in an amount in the range of from about 0.01% to about 50% by weight of the tackifying agent.

56. The particulate slurry of claim 53, wherein the multifunctional material is present in an amount in the range of from about 0.1% to about 1% by weight of the tackifying agent.



**FIGURE 1**



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(54) Abstract Title

**Modified natural particles for fracturing and sand control**

(57) A composition for formation fracturing and sand control includes natural particulate material which has been modified to resist deformation. The natural material can be nut shells, fruit pips and processed woods and the modifying agent may be a silane, siloxane, polyisocyanate or polyepoxy based compounds. The natural materials may be relatively lightweight and neutrally buoyant relative to the carrier fluid.

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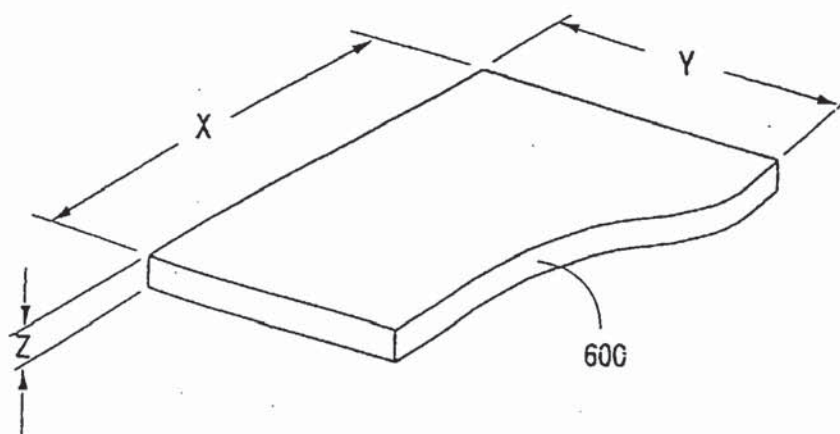


FIG. 1

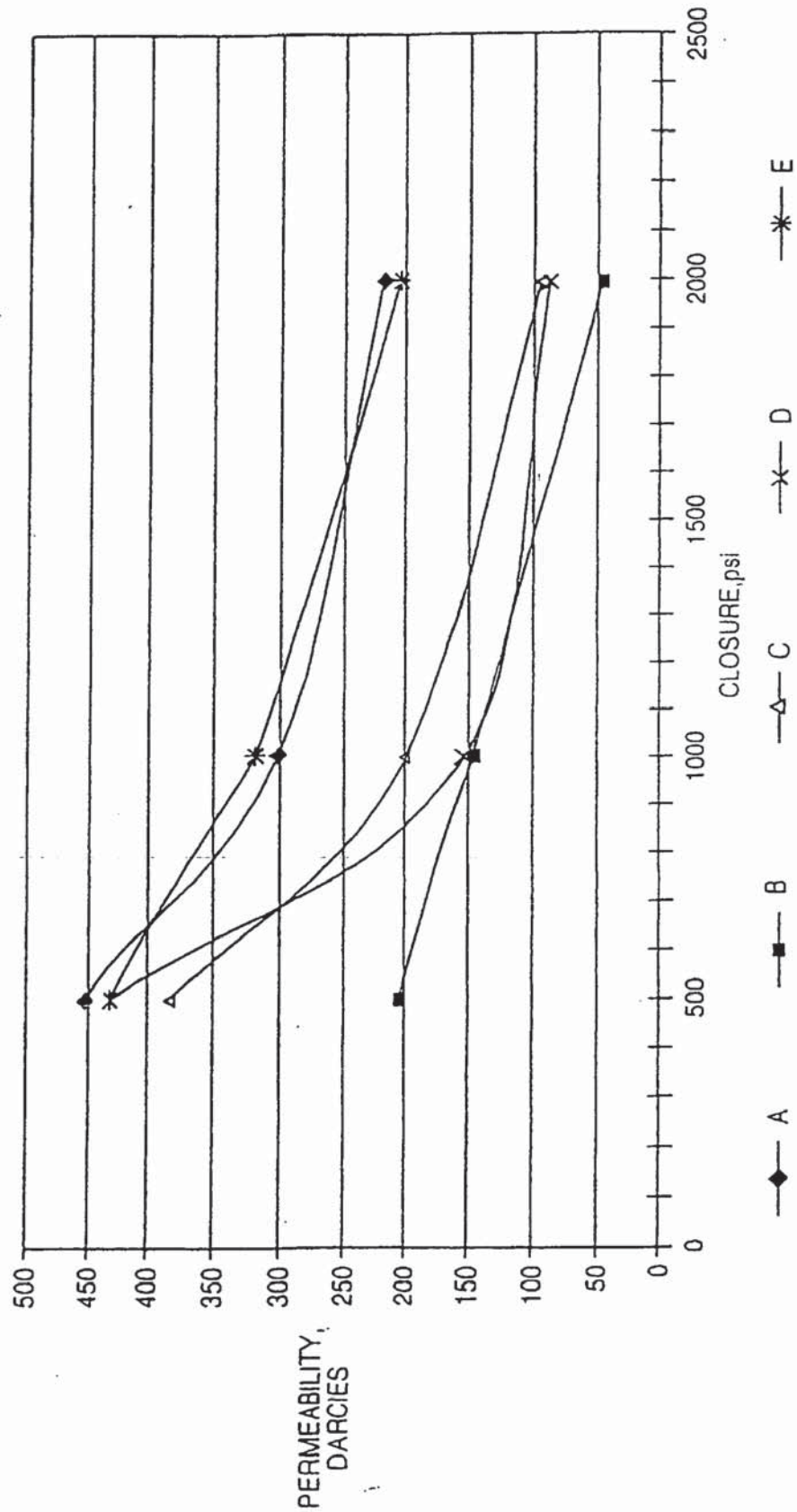


FIG. 2



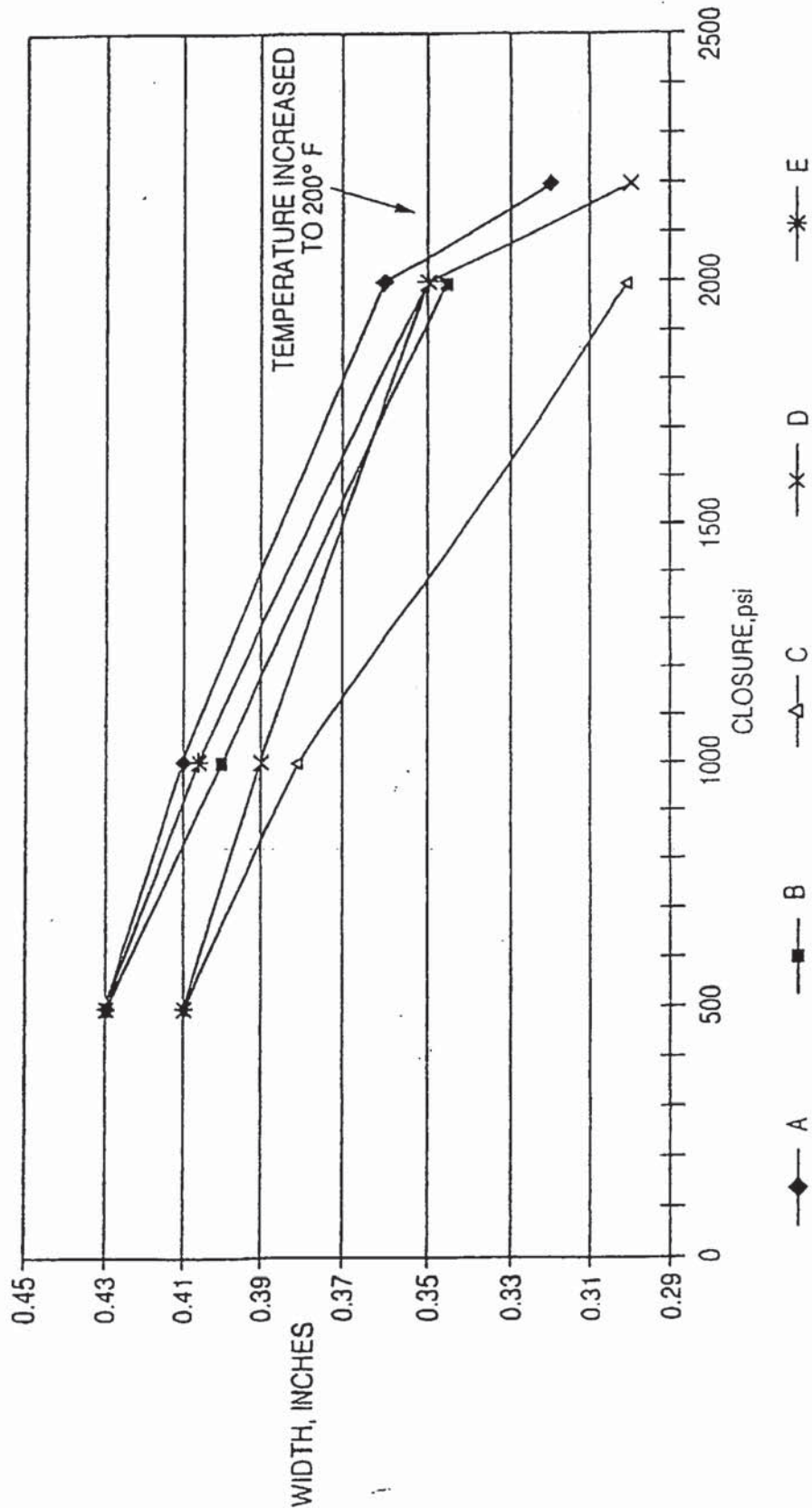


FIG. 3

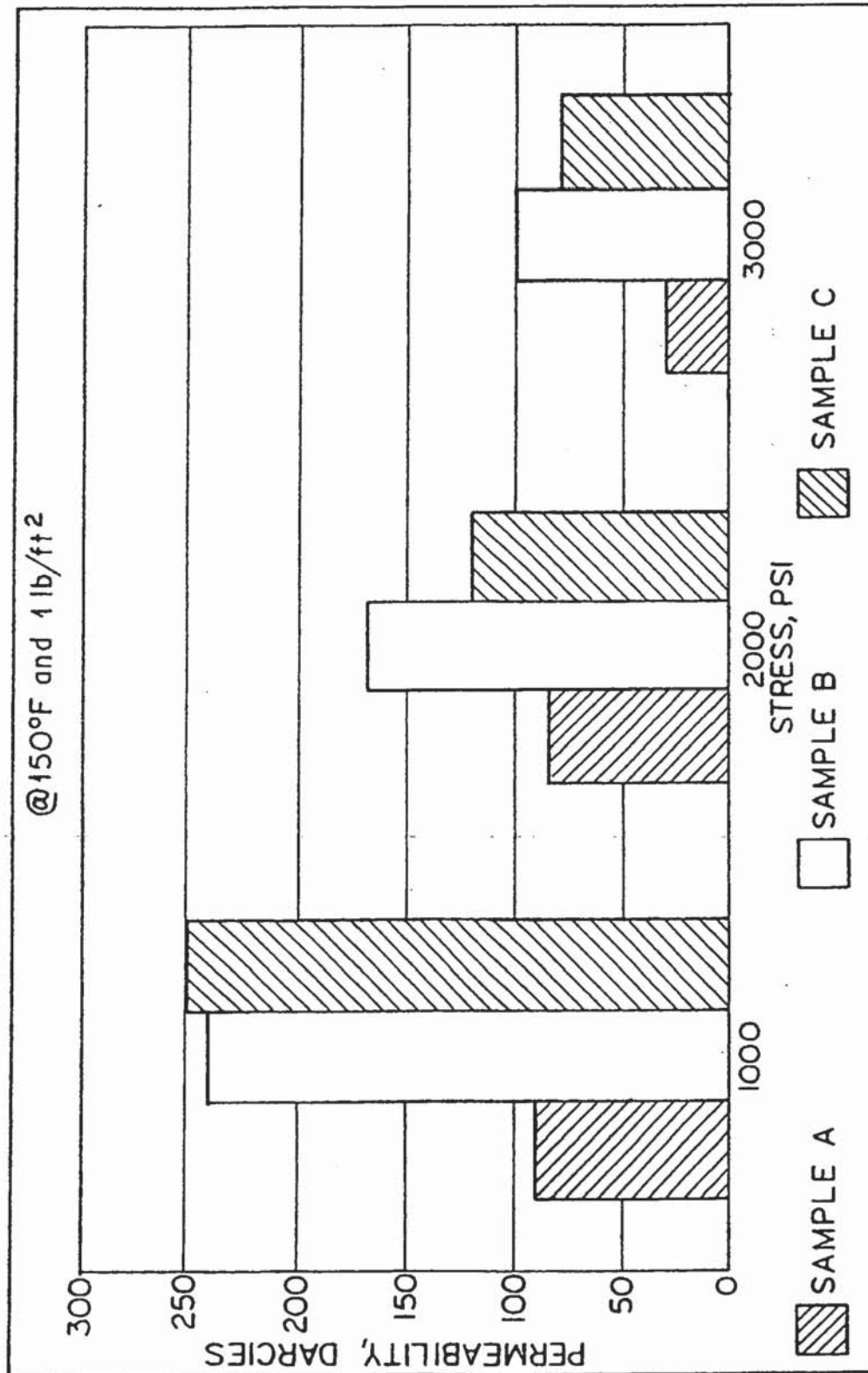


FIG. 4

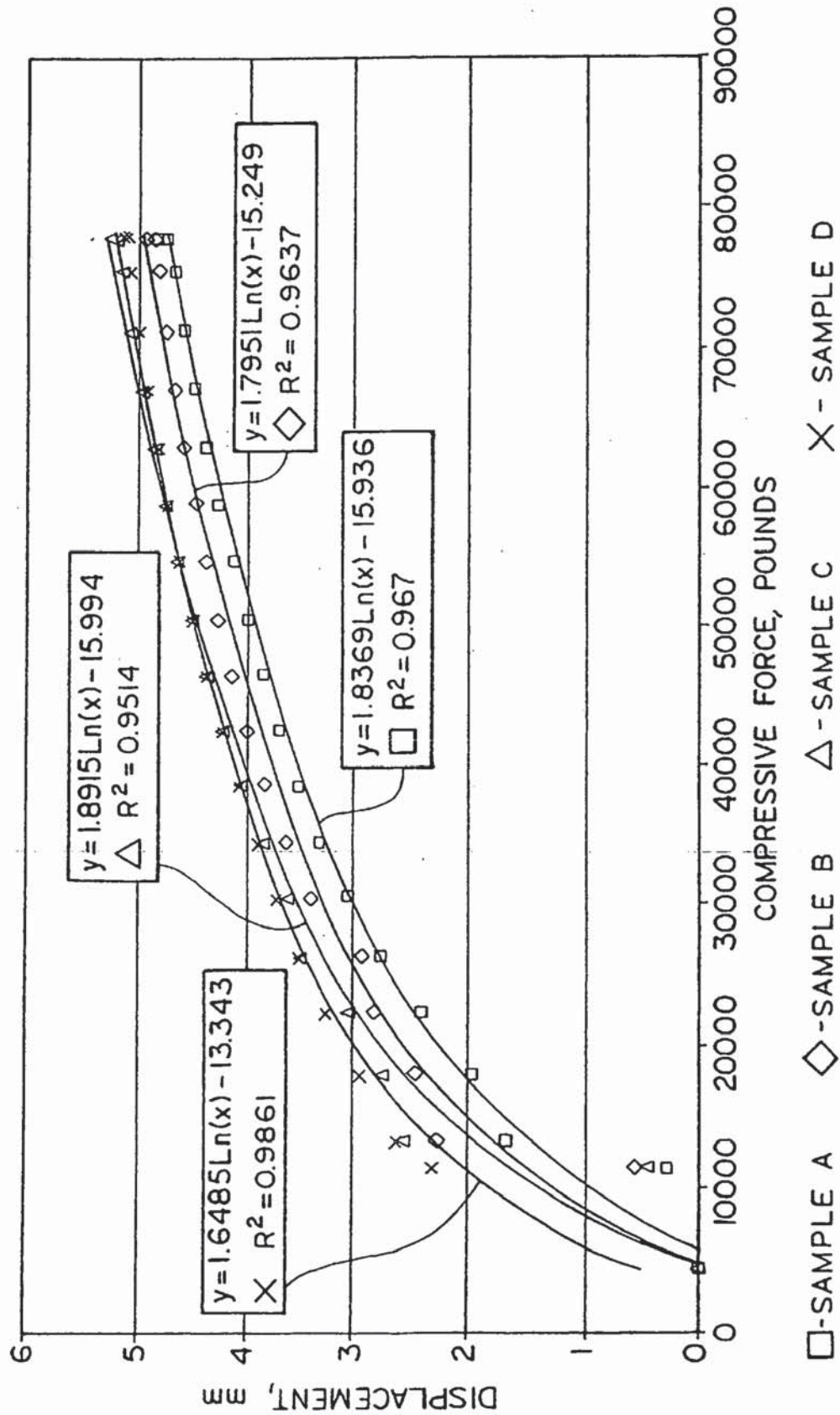


FIG. 5



LIGHTWEIGHT PARTICULATE MATERIALS AND USES THEREFOR  
BACKGROUND OF THE INVENTION

1. Field of the Invention

5

This invention relates generally to methods and compositions useful for subterranean formation treatments, such as hydraulic fracturing treatments and sand control. In particular, this invention relates to use of relatively  
10 lightweight and/or substantially neutrally buoyant particles as proppant material in hydraulic fracturing treatments and as particulate material in sand control methods such as gravel packing, frac pack treatments, etc.

15 2. Description of the Related Art

Hydraulic fracturing is a common stimulation technique used to enhance production of fluids from subterranean formations. In a typical hydraulic fracturing treatment,  
20 fracturing treatment fluid containing a solid proppant material is injected into the formation at a pressure sufficiently high enough to cause the formation or enlargement of fractures in the reservoir. During a typical fracturing treatment, proppant material is  
25 deposited in a fracture, where it remains after the treatment is completed. After deposition, the proppant material serves to hold the fracture open, thereby enhancing the ability of fluids to migrate from the formation to the well bore through the fracture. Because  
30 fractured well productivity depends on the ability of a fracture to conduct fluids from a formation to a wellbore,

fracture conductivity is an important parameter in determining the degree of success of a hydraulic fracturing treatment.

5 Hydraulic fracturing treatments commonly employ proppant materials that are placed downhole with a gelled carrier fluid (e.g., aqueous-based fluid such as gelled brine). Gelling agents for proppant carrier fluids may provide a source of proppant pack and/or formation damage, and  
10 settling of proppant may interfere with proper placement downhole. Formation damage may also be caused by gelled carrier fluids used to place particulates downhole for purposes such as for sand control, e.g., gravel packs, frac packs, etc. Formulation of gelled carrier fluids  
15 usually requires equipment and mixing steps designed for this purpose.

#### SUMMARY OF THE INVENTION

20 In the disclosed method, the application of relatively lightweight and/or substantially neutrally buoyant particulate material as a fracture proppant particulate advantageously may provide for substantially improved overall system performance in hydraulic fracturing  
25 applications, or in other well treating applications such as sand control. By "relatively lightweight" it is meant that a particulate has a density that is substantially less than a conventional particulate material employed in hydraulic fracturing or sand control operations, e.g.,  
30 sand or having a density similar to these materials. By "substantially neutrally buoyant", it is meant that a

particulate has a density sufficiently close to the density of a selected ungelled or weakly gelled carrier fluid (e.g., ungelled or weakly gelled completion brine, other aqueous-based fluid, slick water, or other suitable fluid) to allow pumping and satisfactory placement of the proppant/particulate using the selected ungelled or weakly gelled carrier fluid. For example, urethane resin-coated ground walnut hulls having a specific gravity of from about 1.25 to about 1.35 grams/cubic centimeter may be employed as a substantially neutrally buoyant proppant/particulate in completion brine having a density of about 1.2. It will be understood that these values are exemplary only. As used herein, a "weakly gelled" carrier fluid is a carrier fluid having minimum sufficient polymer, viscosifier or friction reducer to achieve friction reduction when pumped down hole (e.g., when pumped down tubing, work string, casing, coiled tubing, drill pipe, etc.), and/or may be characterized as having a polymer or viscosifier concentration of from greater than about 0 pounds of polymer per thousand gallons of base fluid to about 10 pounds of polymer per thousand gallons of base fluid, and/or as having a viscosity of from about 1 to about 10 centipoises. An ungelled carrier fluid may be characterized as containing about 0 pounds per thousand gallons of polymer per thousand gallons of base fluid.

Advantageously, in one embodiment use of substantially neutral buoyant particulate material may eliminate the need for gellation of carrier fluid, thus eliminating a source of potential proppant pack and/or formation damage. Furthermore, a relatively lightweight particulate material



may be easier to place within a targeted zone due to lessened settling constraints, and a reduced mass of such relatively lightweight particulate material is generally required to fill an equivalent volume than is required  
5 with conventional sand control particulates, used, for example, for gravel packing purposes. Elimination of the need to formulate a complex suspension gel may mean a reduction in tubing friction pressures, particularly in coiled tubing and in the amount of on-location mixing  
10 equipment and/or mixing time requirements, as well as reduced costs. Furthermore, when treated to have sufficient strength (e.g., by substantially filling the permeable porosity of a porous particle with resin or hardener), the disclosed relatively lightweight  
15 proppant/particles may be employed to simplify hydraulic fracturing treatments or sand control treatments performed through coil tubing, by greatly reducing fluid suspension property requirements. Downhole, a much reduced propensity to settle (as compared to conventional proppant  
20 or sand control particulates) may be achieved, particularly in highly deviated or horizontal wellbore sections. In this regard, the disclosed substantially neutral buoyancy proppant/particulate material may be advantageously employed in any deviated well having an  
25 angle of deviation of between about 0 degree and about 90 degrees with respect to the vertical. However, in one embodiment, the disclosed particulate material may be advantageously employed in horizontal wells, or in deviated wells having an angle with respect to the  
30 vertical of between about 30 degrees and about 90 degrees, alternatively between about 75 degrees and about 90

degrees. Thus, use of the disclosed relatively lightweight and/or substantially neutrally buoyant particulate materials disclosed herein may be employed to achieve surprising and unexpected improvements in  
5 fracturing and sand control methodology, including reduction in proppant pack and/or formation damage, and enhancement of well productivity.

In another embodiment, protective and/or hardening  
10 coatings, such as resins described elsewhere herein may be selected to modify or customize the specific gravity of a selected base particulate/proppant material, e.g., ground walnut hulls, etc. Modification of particulate specific gravity (i.e., to have a greater or lesser specific  
15 gravity) may be advantageously employed, for example, to provide proppant or sand control particulates of customized specific gravity for use as a substantially neutrally buoyant particulate with a variety of different weight or specific gravity carrier fluids. In yet another  
20 embodiment, protective and/or hardening-type coatings may be optionally curable to facilitate proppant pack/sand control particulate consolidation after placement. In this regard, curable resins are known to those of skill in the art, and with benefit of this disclosure may be  
25 selected to fit particular applications accordingly.

The disclosed relatively lightweight and/or substantially neutrally buoyant particulate/proppant materials may be employed with carrier fluids that are gelled, non-gelled,  
30 or that have a reduced or lighter gelling requirement as compared to carrier fluids employed with conventional



fracture treatment/sand control methods. In one embodiment employing one or more of the disclosed substantially neutrally buoyant particulate materials and a brine carrier fluid, mixing equipment need only include  
5 such equipment that is capable of (a) mixing the brine (dissolving soluble salts), and (b) homogeneously dispersing in the substantially neutrally buoyant particulate material.

10 In one embodiment, a substantially neutrally buoyant particulate/proppant material may be advantageously pre-suspended and stored in a storage fluid (e.g., brine of near or substantially equal density), and then pumped or placed downhole as is, or diluted on the fly.

15 In one respect, disclosed are well treating methods (e.g., hydraulic fracturing, sand control) that may be employed to treat a well penetrating a subterranean formation, and that include introducing a relatively lightweight and/or  
20 substantially neutral density particulate/proppant material into the well. Individual particles of the particulate material optionally may have a shape with a maximum length-based aspect ratio of equal to or less than about 5. Individual particles may also be optionally  
25 coated with protective materials such as resins and/or hardeners, for example, "2AC" phenol formaldehyde hardener from BORDEN CHEMICAL. Examples of suitable relatively lightweight and/or substantially neutrally buoyant materials for use in aqueous based carrier fluids include,  
30 but are not limited to, ground or crushed nut shells, ground or crushed seed shells, ground or crushed fruit



pits, processed wood, or a mixture thereof. Optional protective coatings for coating at least a portion of individual particles of such relatively lightweight and/or substantially neutrally buoyant materials include, but are not limited to at least one of phenol formaldehyde resin, melamine formaldehyde resin, urethane resin, or a mixture thereof. Other optional coating compositions known in the art to be useful as hardeners for such materials (e.g., coating materials that function or serve to increase the elastic modulus of the material) may be also employed in conjunction or as an alternative to protective coatings, and may be placed underneath or on top of one or more protective coatings. It will be understood by those of skill in the art that such protective and/or hardening coatings may be used in any combination suitable for imparting desired characteristics to a relatively lightweight and/or substantially neutrally buoyant particulate/proppant material, including in two or more multiple layers. In this regard successive layers of protective coatings, successive layers of hardening coatings, alternating layers of hardening and protective coatings, etc. are possible. Mixtures of protective and hardening coating materials may also be possible.

25 In another respect, disclosed is a relatively lightweight and/or substantially neutrally buoyant fracture proppant/particulate material for use in a hydraulic fracturing/sand control treatment that is a ground or crushed walnut shell material that is coated with a resin to substantially protect and water proof the shell. Such a material may have a specific gravity of from about 1.25

to about 1.35, and a bulk density of about 0.67. In one exemplary case, size of such a material may be about 12/20 US mesh size. In another exemplary case, sizes may range from about 4 mesh to about 100 mesh. Advantageously, in some embodiments, such ground walnut shells may serve to attract fines and formation particles by their resinous nature. In one embodiment for the manufacture of such particles for proppant/sand control applications, an optional hardener may be applied to a ground walnut shell material first followed by a urethane coating as described elsewhere herein that may vary in amount as desired. For example, such a coating material may be present in an amount of from about 1% to about 20%, alternatively from about 10% to about 20% by weight of total weight of individual particles. Alternatively, such a coating material may be present in an amount of from about 2% to about 12% by weight of total weight of individual particles. Amount of resin may depend, for example, on price and application. In this regard, particulates may be first sprayed or otherwise coated with a hardener, and a coating may be applied to be about 12% by weight of total weight of the particle.

In a further embodiment, individual particles (e.g., granules) of naturally-occurring materials (e.g., made from naturally-occurring materials or derivatives of naturally-occurring materials including, but not limited to, plant-based or agricultural-based materials such as nut hulls, seed shells, processed wood materials, derivatives of such plant-based or agricultural-based materials, etc.) may be optionally treated by exposure to



a modifying agent that is capable of interacting with compounds present in or on a natural material in a way that acts to increase the ability of the naturally-occurring material to resist deformation (e.g., by  
5 increasing the elastic modulus or otherwise strengthening and/or, hardening the naturally-occurring material). Examples of suitable modifying agents include, but are not limited to, any compound or other material capable of modifying (e.g., crosslinking, coupling or otherwise  
10 reacting with) one or more components present in the naturally-occurring material (e.g., natural resins, lignins and/or cellulosic fibers). Specific examples of suitable modifying agents include, but are not limited to, agents including polyisocyanates, silanes, siloxanes, and  
15 combinations thereof. Selected modifying agent/s may be advantageously used to increase the elastic modulus of a given naturally occurring material, for example, to make particles of a given naturally-occurring material more suitable (e.g., having increased hardness or strength to  
20 resist or prevent deformation under downhole *in situ* conditions of formation temperature and formation closure stress) for use as a relatively lightweight and/or substantially neutrally buoyant fracture proppant or sand control particulate material having increased  
25 effectiveness when exposed to higher closure stresses or other mechanical stresses that may be encountered downhole during a well treatment such as a hydraulic fracturing or sand control treatment.

30 Effectiveness of modifying agents may be optionally enhanced, for example, by facilitating interaction between



a modifying agent and one or more components present in a naturally occurring material. In this regard interaction between a modifying agent and components present in a naturally occurring material may be facilitated using one  
5 or more enhancing agents (e.g., swelling agents, penetrating agents, etc.) and/or by exposing a naturally occurring material to one or more interaction-enhancing conditions that serve to enhance interaction with a modifying agent (e.g., vacuum and/or pressure impregnation  
10 of the modifying agent into a naturally occurring material, etc.). Examples of suitable enhancing agents include, but are not limited to, liquid or gaseous ammonia, dimethyl sulfoxide ("DMSO"), methyl pyrrolidone, etc.

15

Thus, disclosed herein is a method for forming modified and strengthened particles of naturally-occurring material that may be used as relatively low density proppant or sand control particulate for fracturing or gravel packing.  
20 In one exemplary embodiment, the modifying process may include exposing particles of the naturally-occurring material to a modifying agent (e.g., that includes an aqueous mixture of alkyl silanes, such as aminopropyltriethoxy silane) to strengthen the naturally-  
25 occurring material against deformation under closure stress. The modifying agent may be exposed to the naturally-occurring materials using any suitable method, including soaking or spraying, and may be allowed to interact or react with the naturally-occurring material  
30 with or without heating. The particles of naturally-occurring material may also be optionally exposed to an

enhancing agent (e.g., liquid ammonia) to allow deeper penetration and interaction of the modifying agent with components of the naturally-occurring material, thus providing more uniform crosslinking or coupling of these  
5 components with less modifying agent and also helping to minimize or avoid localized crosslinking or coupling within the particles. A coating or layer of a material such as resin or epoxy may be added after treatment with a modifying agent to further enhance or increase strength of  
10 the naturally-occurring material, and/or to minimize downhole fluid incompatibilities.

Also disclosed herein is a method of using modified particles of naturally-occurring material as a relatively  
15 lightweight particulate material that may be introduced as part of a treating fluid into a well down wellbore tubulars (e.g., tubing, workstring, casing, drillpipe) or down coiled tubing, for example at concentrations of about 0.25 to about 15 pounds per gallon of treating fluid. In  
20 one exemplary embodiment, specific gravity of the particles of modified naturally-occurring material may be about 1.3, and therefore they may be used as a substantially neutrally buoyant proppant or sand control particulate in light or heavy brines, thus eliminating the  
25 need for complex crosslinked fracturing or sand control carrier fluids.

In one embodiment, the disclosed relatively lightweight particulate/proppant material may be introduced or pumped  
30 into a well as neutrally buoyant particles in, for example, a saturated sodium chloride solution carrier

fluid or a carrier fluid that is any other completion or workover brine known in the art, for example, having a specific gravity of from about 1 to about 1.5, alternatively from about 1.2 to about 1.5, further  
5 alternatively about 1.2, thus eliminating the need for damaging polymer or fluid loss material. In one embodiment, such a material may be employed as proppant/sand control particulate material at temperatures up to about 150°F, and pressures up to about 1500 psi.  
10 However, these ranges of temperature and closure stress are exemplary only, it being understood that the disclosed materials may be employed as proppant/sand control materials at temperatures greater than about 150°F and/or at closure stresses greater than about 1500 psi. For  
15 example, particles of naturally-occurring material may be exposed to suitable modifying agents, with or without enhancing agents and/or conditions, in one embodiment to form relatively lightweight particulate material that may be employed as proppant or sand control particulate at  
20 temperatures up to about 300°F, and/or at closure stresses up to about 10,000 psi, with temperatures greater than about 300°F and/or closure stresses greater than about 10,000 psi also being possible. In any event, it will be understood with benefit of this disclosure that core  
25 and/or layer material/s (when present) and/or interaction-enhancing materials/conditions may be selected by those of skill in the art to meet and withstand anticipated downhole conditions of a given application.

30 Advantageously, in one embodiment the low specific gravity of the relatively lightweight proppant material may be



taken advantage of to result in a larger fracture or frac  
pack width for the same loading (i.e., pound per square  
foot of proppant) to give much larger total volume and  
increased width for the same mass. Alternatively, this  
5 characteristic allows for smaller volumes of proppant  
material to be pumped while still achieving an equivalent  
width.

In one respect, disclosed herein is a method for treating  
10 a well penetrating a subterranean formation, including  
introducing a particulate material into the well. In this  
method, at least a portion of the particulate material may  
include particles of a naturally-occurring material  
modified by exposure to at least one modifying agent, the  
15 modifying agent being effective to modify the naturally-  
occurring material by increasing the ability of the  
naturally-occurring material to resist deformation.

In another respect, disclosed herein is a method of  
20 fracturing a subterranean formation, including introducing  
a particulate material suspended in a carrier fluid into  
the subterranean formation at a pressure above a  
fracturing pressure of the subterranean formation. In  
this method, at least a portion of the individual  
25 particles of the particulate material may be substantially  
neutrally buoyant in the carrier fluid and may include  
particles of a naturally-occurring material modified by  
exposure to at least one modifying agent in an amount  
effective to modify the naturally-occurring material. At  
30 least a portion of individual particles of the modified  
naturally-occurring material may include at least one of