Title: METHOD FOR MAKING MODIFIED PROPPANTS AND THEIR USE FOR HYDRAULIC FRACTURING

Abstract: Method of making proppants modified with certain organosilanes, modified proppants obtainable by such process and the use of such modified proppants for fracturing. Preferably, the proppants are omniphobic proppants.
Method for making modified proppants and their use for hydraulic fracturing

The invention relates to a method of making proppants modified with certain organosilanes, modified proppants obtainable by such process and the use of such modified proppants for hydraulic fracturing. In a preferred embodiment of the invention the proppants are omniphobic proppants.

Hydraulic fracturing is a method of increasing the permeability of subterranean oil- and/or gas-bearing formations. In hydraulic fracturing operations aqueous formulations, so called fracturing fluids, are injected through a wellbore into a subterranean formation at a pressure sufficient to create fractures, fissures and the like in such subterranean formations.

In order to avoid that fractures formed by hydraulic fracturing close after release of the pressure fracturing fluids usually comprise proppants. Proppants are small particles having a typical particle size from a few hundred µm to a few mm which are added to the fracturing fluid and are carried by the fracturing fluids to the fractures formed. When releasing the pressure the proppants remain in the fractures and keep the fractures open. Examples of proppants include inorganic materials such as natural quartz sand, glass particles, ceramic particles but also particles of synthetic or natural polymers or natural materials such as crushed nut-shells.

It is known in the art to coat proppant particles in order to modify its properties. Proppants may be coated with hydrophobic materials, such as polymer coatings or coating with siloxanes. Such a coating may ease the removal of the fracturing fluid form the formation after hydraulic fracturing.

US 2005/0244641 A1 discloses a proppant comprising essentially spherical particles which are coated with hydrophobic materials such as silicones, siloxanes, teflon, plant oils, hydrocarbons, copolymerized polyvinylidene chloride, glass frit and enamel.

US 2010/0167965 A1 discloses a method of fracturing subterranean formations by coating particles with an amphiphobic coating to form amphiphobic proppants and to inject such amphiphobic particles together with a carrier fluid into the formation. A wide variety of materials such as fluoropolymers, tetrafluorethylene/vinylether copolymers, Teflon or other fluorinated compounds may be used for the amphiphobic coating.

WO 2013/049235 A1 discloses a proppant comprising a multi-shell structure comprising a substrate material, a polymeric material disposed on the substrate material and a surface wettability modifier disposed on the polymeric material. The wettability modifier may be selected from the group of polydimethylsiloxanes, polyalkyleneoxidemethylsiloxane copolymers, 2-hydroxy ethyl methacrylate, tridecafluoroocctyltriethoxysilane or heptadecafluorodecytrimethyltrimethoxysilane.

US 2013/029218 A1 discloses a method of hydraulic fracturing in which proppant particles are used which have a surface that is both hydrophobic and oleophobic. The proppants comprise at least a partial coating of fluoroalkyl-functional organopolysiloxanes, poly(perfluoroalkyl ethyl
methacrylate), polyfluoroacrylate, fluorinated oxetane co- or terpolymers, fluorinated resins, polyvinylfluoride, or fluoroalkyl-polyurethane copolymers.

There are also other techniques of hydraulic fracturing known in the art in which organosilanes are used.

US 2009/0264323 A1 discloses a process for the preparation of consolidated proppants by mixing a consolidation agent with a proppant and curing the consolidation agent mixed with the proppant at elevated pressure and at elevated temperature. The consolidation agent is a hydrolysate or condensate of at least one functionalized organosilane. The function of the organosilanes is not to coat particles but they act as a binder to consolidate proppants.

US 2010/0163234 A1 discloses a method of treating a subterranean formation with a fluid comprising a proppant and a organosilane \( R_nSiX_{4-n} \) and introducing such fluid into the formation. In the formation the organosilanes modify the wettability of the proppant and/or the formation itself. In the method disclosed, not pre-coated proppants are injected but the fluid injected coats surfaces in the formation and/or proppants are coated in-situ in the formation.

The coatings of proppants must be stable under the conditions prevailing in hydraulic fracturing operations. There is still a need for providing proppants having a stable coating.

It was an object of the present invention to provide proppants having a hydrophobic or omni-phobic (both hydrophobic and oleophobic) coating with high stability.

Correspondingly, a method for making modified proppants for hydraulic fracturing having a hydrophobic surface has been found by providing unmodified proppants and coating the unmodified proppants with at least one organosilane,

wherein

- the unmodified proppants comprise an inorganic material comprising at least Si-atoms and/or Al-atoms and oxygen atoms, and
- the unmodified proppants comprise X-O-H groups at their surface, wherein X is selected from the group of Si, Al or other at least bivalent metal ions,
- the organosilanes are selected from the group of

\[
\begin{align*}
R SiY \quad & (1) \\
RsSiY \quad & (2) \\
R_3SiQSiR \quad & (3) \\
Y_3Si-C_nH_{2n-C_mF_{2m+1}} \quad & (4),
\end{align*}
\]

wherein

- \( R \) is a hydrophobic organic group which does not undergo hydrolysis in the presence of water,
Q is selected from the group of >NH, >PH, -S- or -O-,
Y is a hydroxyl or a hydrolysable group, and
n is from 0 to 5 and m is from 1 to 12,
and wherein the surface X-O-H groups react with the organosilanes to form X-O-Si bonds.

In a preferred embodiment, the method includes pretreating the unmodified proppants with an aqueous solution of a base.

In a further embodiment, the invention relates to the use of proppants according obtainable by sais method for hydraulic fracturing comprising at least the steps of

- providing an aqueous fracturing fluid comprising at least water and a proppant according to claims 14 or 15,
- injecting the aqueous fracturing fluid through a wellbore into a subterranean formation at a pressure sufficient to create fractures into the subterranean formation.

List of figures:

Figure 1  Schematic representation of direct coating of unmodified proppants with organosilanes (method 1)

Figure 2  Schematic representation of coating of unmodified proppants with organosilanes using a sol-gel process (method 2)

Specific details of the invention are as follows:

The proppants of the present invention comprise a core comprising at least one inorganic material and a hydrophobic, preferably omniphobic coating which is covalently bonded to the core. They are made by modifying unmodified proppants, i.e. proppants which do not yet comprise a coating, with organosilanes.

The unmodified proppants comprise an inorganic material comprising at least Si-atoms and/or Al-atoms and oxygen atoms, i.e. the materials are oxidic materials. The unmodified proppants may comprise Si- and/or Al-oxides and optionally further oxides such as iron oxides or titanium oxides. The Al- and/or Si-compounds may also be silicates and/or aluminates and may comprise further cations as counter ions. Examples of such materials comprise natural materials such as sand or natural silicates or man-made materials such as ceramic particles based on alumina, bauxite, silicon dioxide or alumosilicates. The unmodified proppants are preferably spherical or at least essentially spherical. The diameter of the particles may be from 0.2 mm to 3 mm, preferably 0.25 mm to 2.5 mm, for example 0.3 mm to 2 mm. In case of non-spherical particles the diameter refers to the longest diameter. The unmodified proppants used for making
the coated, modified proppants according to the present invention comprise X-O-H groups at the surface, wherein X is a least is at least one selected from the group of Si, Al, or other at least bivalent metal ions that form the proppants matrix.

The surface modification is achieved by reacting suitable organosilanes with surface X-OH groups of the proppant forming strong X-O-Si-covalent bond.

In a preferred embodiment of the present invention the unmodified proppant core particles optionally may be pretreated with an aqueous solution of a base, preferably a strong base to activate its surface by creating more surface X-OH groups before reacting them with the organosilanes. Examples of suitable bases include inorganic bases such as KOH and NaOH or organic bases such as ammonia, amines and quinidine. The pretreatment may be performed by soaking the proppant in the base solution at temperature from 20°C to 100°C, preferably 20°C to 80°C for 1 to 24 hours. After the pretreatment should be washed to remove the base and thereafter dried at temperatures not exceeding 100°C, preferably not exceeding 80°C. Drying may preferably be performed at reduced pressures.

For modifying the surface of the unmodified proppants at least one organosilane selected from the group of

\[ RSiYs \]  \hspace{1cm} (1)
\[ R_3SiY \]  \hspace{1cm} (2)
\[ R_3Si-Q-SiR_3 \]  \hspace{1cm} (3)
\[ Y_3Si-C_nH_{2n}-C_mF_{2m+1} \]  \hspace{1cm} (4)

is used. Of course a mixture of two or three different organosilanes (1) to (4) may be chosen.

In the formulas (1) to (4) the moieties \( R \) represent independently from each other- a hydrophobic organic group which does not undergo hydrolysis in the presence of water.

Preferably \( R \) is a hydrocarbon group having from 1 to 30 carbon atoms, preferably 1 to 18 carbon atoms wherein the H atoms of the hydrocarbon group may be completely or incompletely substituted by halogen atoms, in particular F and/or Cl atoms. The hydrocarbon group may be a linear or branched, saturated or unsaturated aliphatic group, a cycloaliphatic group or an aromatic group, wherein cycloaliphatic or aromatic groups may be further substituted by linear and/or branched aliphatic groups.

In one embodiment of the invention the hydrocarbon groups \( R \) are linear or branched alkyl groups \( R_1 \) having from 1 to 18 carbon atoms. Examples of such alkyl groups comprise methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, tert-pentyl, n-hexyl, n-heptyl, n-octyl, n-neptyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl and n-octadecyl groups.
In another embodiment of the invention the hydrocarbon groups R are substituted or unsubstituted cycloaliphatic groups R² having 5 to 12 carbon atoms. Examples of such cycloaliphatic groups comprise cyclopentyl, cyclohexyl, or cycloheptyl groups.

In another embodiment of the invention the hydrocarbon groups R are linear or branched alkenyl groups R³ having 2 to 18 carbon atoms. Examples comprise vinyl, propenyl, butenyl, hexenyl, or octenyl groups.

In another embodiment of the invention the hydrocarbon groups R are substituted or unsubstituted aryl groups R⁴ having 5 to 18 carbon atoms, preferably 6 to 8 carbon atoms. Examples comprise phenyl, halide-phenyl, benzyl, halide-benzyl, phenylethyl, halide-methyl phenyl or halide-ethyl phenyl groups.

In structures (1) and (2) Y is a hydroxy group or a hydrolysable group. The term hydrolysable group refers to a group that is capable of undergoing hydrolysis and polycondensation in the presence of water.

Preferably Y is selected from hydroxy, methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, n-hexoxy, n-octoxy, n-decoxy, n-dodecoxy, n-hexadecoxy, n-octadecoxy, n-cyclohexoxy, vinoxy, phenoxy, benzoxy, phenylethoxy, halide methoxy, F, Cl, Br and I, more preferably from the group of methoxy, ethoxy, and Cl. Preferably all groups Y in one molecule are the same.

If R is an alkyl group R¹ then Y is preferably an alkoxy group, in particular methoxy or ethoxy.

In formula (3) Q is selected from the group of >NH, >PH, -S- or -O-. Preferably Q is NH.

The organosilanes of formula (4) comprise a fluorine substituted alkyl group wherein n is from 0 to 5 and m is from 1 to 12. Preferably, n is 0, 1 or 2 and m is 1, 2, 3, 4, 5 or 6 with the proviso that the sum n + m is from 2 to 16.

Examples of preferred structures (1) comprise organosilanes of the formula R¹SiY³ (1a) wherein the alkyl group R¹ has 4 to 22, preferably 6 to 20, more preferably 8 to 18 carbon atoms and Y is a group selected from methoxy and ethoxy.

Examples of preferred structures (3) comprise organosilanes of the formula R¹3Si-NH-SiR³ (3a), wherein the alkyl group R¹ has 1 to 4, preferably 1 or 2 carbon atoms.

Examples of preferred structures (4) comprise organosilanes in which the sum of n+m is 6 to 12, n is 1 to 4, preferably 2, and m is 4 to 8, preferably 6.
In one embodiment of the invention, the modification of the surface of the unmodified proppants may be performed by direct grafting of the organosilanes onto the proppant surface via condensation reaction between the -Si-Y groups of the organosilanes with surface X-OH (method 1) groups of the unmodified proppant establishing X-O-Si linkage. The compound (3) reacts with surface X-OH group forming X-O-SiR3 and HQ-SiR3 as a leaving group. The HQ-SiR3 may further react with other X-OH group to form another X-O-SiR3 and H2O as leaving group. Similar reaction takes place when Q = O, however at lower rate and required higher temperature. The Si-Q-Si bonds cleave when it react with surface X-OH groups and form H2O as final leaving group.

As already mentioned above it is preferred to activate the surface of the proppant before reacting them with the organosilanes in order to generate surface X-OH groups. The grafting reaction may be performed in a nonpolar organic solvent capable of solving and/or dispersing the organosilanes at temperature from at temperature from 20 °C to 100 °C for 1 to 24 hours. For performing the modification, the proppants may be dispersed in at least one nonpolar organic solvent followed by the addition of at least one organosilane (1) to (4). Examples of preferred organic solvents include aliphatic, alicyclic, aromatic hydrocarbon solvents and/or their halogenated derivatives. Preferably the boiling point of the solvent is 40°C to 140°C. The principles of method 1 are illustrated in figure 1. Method 1 is applicable for the organosilanes (1) to (4).

In another embodiment (method 2) of the invention the surface functionalization of the unmodified proppant may be performed surface using a sol-gel coating technique. In this method the organosilanes are pre-hydrolyzed and pre-condensed in a solvent in the presence of water and optionally a catalyst to form a short organosiloxane network. The short organosiloxane network then reacts with proppant surface X-OH groups forming a coating layer through X-O-Si linkages. The sol-gel process is performed in a solvent capable solving and/or dispersing the organosilanes used. In principle the solvent may be any solvent suitable for performing sol-gel processes with organosilanes except for water which is a reactant in the sol-gel process. Suitable solvents lead to a homogenous solution or dispersion of the reactive components hence a precipitation or macrophase separation is to be avoided. The solvent also should dissolve water in an amount of at least 1 to 10 grams water per 100 g solvent. The boiling temperature of the solvent is preferably from 40°C to 140°C. Suitable solvents may be selected from monofunctional alcohols or multifunctional alcohols, in particular diols and triols, ethers such as tetrahydrofuran, ketones such as acetone, methyl ethyl ketone, methyl-n-propyl methyl-n-butyl ketone, diethyl ketone, methyl-iso-butyl ketone, methyl-n-pentyl ketone, ethyl-n-butyl ketone, and methyl-n-hexyl ketone. In principle any catalyst suitable for catalyzing the hydrolysis of organosilanes may be used for the sol-gel process. Suitable catalysts are in particular acids and bases. Preferred acids are strong acids such as a mineral acid or an organic acid. Suitable bases are in particular tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide and tetrabutyl ammonium hydroxide. A person skilled in the art is aware that the nature of the catalyst chosen influences the structure of the silica network obtained by sol-gel processes in general such as for instance disclosed in Banker et al., Sol-Gel Science, Academic Press, San Die...
go, Calif. (USA) 1990. The amount of water preferably is selected such that the molar ratio of water to Si is from 1 to 10, particularly preferred from 2 to 6. The molar ratio of organosilane to the solvent can range from approximately 1:1 to approximately 1:100, preferably from 1:2 to 1:20, in particular from 1:5 to 1:12, very particularly preferred from 1:7 to 1:11. The amount of acid is preferably selected such that the molar ratio of hydrolysable, i.e., active protons to the total number of silicon atoms in the organosilanes is from 0.0005 to 0.01. Preferably, the pH value of the resulting reaction mixture is from 0.5 to 5, in particular from 1 to 4 determined at the beginning of the reaction. The duration of pre-hydrolization and pre-condensation step can range ranges from 1 minute to 24 hours. The temperature typically ranges from 20°C to 100°C.

Method 2 is applicable for forming a sol-gel coating on proppant surfaces with organosilanes (1) and (4) or mixtures thereof.

In a preferred embodiment of the invention, the unmodified proppant particles are coated with organosilanes (4). Such a surface modification has the advantage that omniphobic proppants are obtained, i.e. proppants with are both, hydrophobic and oleophobic.

In one embodiment, the invention relates to proppants having a hydrophobic surface obtainable by the method as described above. In the embodiment, organosilanes (1) to (4) may be used.

In one further embodiment, the invention relates to proppants having an omniphobic surface obtainable by the method as described above and using at least one organosilane (4) in the method.

The modified proppants obtainable by the method described above may be used in a method of hydraulic fracturing subterranean formations.

For hydraulic fracturing a fracturing fluid at least comprising a solvent or a mixture of different solvents and a proppant according to the present invention are used. Preferably, the fracturing fluid is an aqueous fracturing fluid and more preferably only water is used as a solvent for the fracturing fluid. The fracturing fluid may comprise additional components such as thickeners such as thickening polymers or viscoelastic surfactants, fluid loss control agents, pH control agents, surfactants, chelating agents, crosslinkers, breakers, biocides, friction reducers. The skilled artisan may make a suitable choice according to his/her needs.

As proppant at least one proppant according to the present invention is used. Of course a mixture of two or three different proppants according to the invention or a mixture with other proppants may be used.

For the hydraulic fracturing the fracturing fluid is injected through a wellbore into a subterranean formation at a pressure sufficient to create fractures into the subterranean formation. The prop-
The following examples are intended to illustrate the invention in detail:

Materials used:

Organosilanes

Octadecyltriethoxysilane \( \text{C}_{18}\text{H}_{37}-\text{Si(OC\text{H}_3)_3} \) type (1)

Hexamethyldisilazane \( (\text{H}_3\text{C})_3\text{Si-NH-Si(CH}_3)_3 \) type (3)

Tridecafluorotetrahydrooctyltriethoxysilane \( \text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{Si(OC\text{H}_5)_3} \) type (4)

Proppants

Proppant 1 Glass particles having a diameter of \( \sim 0.2 \) to \( 0.3 \) (Silibead\textsuperscript* type S, Sigmund Lindner GmbH)

Proppant 2 Ceramic particles of an alumosilicate \( (~ 51 \% \text{ by wt. } \text{Al}_2\text{O}_3, ~ 45 \% \text{ SiO}_2, ~ 2 \% \text{ TiO}_2, ~ 1 \% \text{ Fe}_2\text{O}_3, ~ 1 \% \text{ others} \) having a diameter of \( \sim 1 \text{ mm} \) (Carbolite\textsuperscript®, Carbo Ceramics, Houston, TX, USA)

Examples 1 to 3:

One gram of proppant 1 was dispersed in 10 mL 1 M NaOH solution and stirred at room temperature for 24 hours for surface activation to create more -Si-OH groups on the surface. The activated glass particle was collected by filtration, washed with water several times until the filtrate show pH around 7 and finally dried at 80°C under vacuum.

The activated and dried glass particles were dispersed in 10 mL anhydrous toluene followed by addition of 0.2 gram of the respective organosilane. The mixture was heated thereafter to reflux under nitrogen atmosphere for 6 hours with continuous stirring. After the reaction, the mixture was cooled down to room temperature, the surface modified glass particles were collected by filtration, washed a few times with toluene and finally dried at 80°C under vacuum.

Examples 4 to 5:

One gram of proppant 2 was dispersed in 10 mL 1 M NaOH solution and stirred at room temperature for 24 hours for surface activation to create more -Si-OH groups on the surface. The
activated glass particle was collected by filtration, washed with water several times until the filtrate show pH around 7 and finally dried at 80 °C under vacuum. The activated and dried ceramic particles were dispersed in 10 mL anhydrous toluene followed by addition of 0.2 gram of the respective organosilane. The mixture was heated thereafter to reflux under nitrogen atmosphere for 6 hours with continuous stirring. After the reaction, the mixture was cooled down to room temperature, the surface modified glass particles were collected by filtration, washed a few times with toluene and finally dried at 80 °C under vacuum.

Test of the surface modified proppants
The surface modified proppants were tested with respect to their wettability by water and by oil. For this purpose a petri dish was filled with a layer of the modified proppants to be tested. Thereafter dodecane (as model oil) and water was dropped on the proppant layer and it was observed whether the liquids were absorbed in the proppant layer or remained as a drop on top of the proppant layer. Depending on the results, the modified proppants were classified as follows:

<table>
<thead>
<tr>
<th></th>
<th>absorbed</th>
<th>not absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>oil (dodecane)</td>
<td>oleophilic</td>
<td>oleophobic</td>
</tr>
<tr>
<td>water</td>
<td>hydrophilic</td>
<td>hydrophobic</td>
</tr>
</tbody>
</table>

Figure 3 comprises a representation of the test. The following table 1 summarizes the results:

<table>
<thead>
<tr>
<th>No.</th>
<th>Particle</th>
<th>Organosilane</th>
<th>hydrophobic</th>
<th>oleophobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Proppant 1 (glass)</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>1</td>
<td>Proppant 1 (glass)</td>
<td>octadecyltriethoxysilane</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>2</td>
<td>Proppant 1 (glass)</td>
<td>hexamethylidisilazane</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>3</td>
<td>Proppant 1 (glass)</td>
<td>tridecafluorotetrahydro-octyltriethoxysilane</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>C2</td>
<td>Proppant 2 (ceramic)</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>4</td>
<td>Proppant 2 (ceramic)</td>
<td>octadecyltriethoxysilane</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>5</td>
<td>Proppant 2 (ceramic)</td>
<td>tridecafluorotetrahydro-octyltriethoxysilane</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 1: Result of the wettability tests

The results show that the surface modification of both glass particles (proppant 1) and ceramic particles (proppant 2) with octadecyltriethoxysilane, hexamethylidisilazane and tridecafluorotetrahydrooctyltriethoxysilane resulted in a hydrophobic surface which is not wetted by water.

Coating of proppant 1 and proppant 2 with tridecafluorotetrahydro-octyltriethoxysilane yielded omnophobic particles, i.e. particles which are both, hydrophobic and oleophobic.
Claims:

1. Method for making modified proppants for hydraulic fracturing having a hydrophobic surface by providing unmodified proppants and coating the unmodified proppants with at least one organosilane, wherein
   • the unmodified proppants comprise an inorganic material comprising at least Si-atoms and/or Al-atoms and oxygen atoms, and
   • the unmodified proppants comprise X-O-H groups at their surface, wherein X is selected from the group of Si, Al or other at least bivalent metal ions,
   • the organosilanes are selected from the group of
     \[ \text{RSiYs} \quad (1) \]
     \[ \text{RsSiY} \quad (2) \]
     \[ \text{RsSi-Q-SiRs} \quad (3) \]
     \[ Y_2Si-C_nH_{2n}-C_mF_{2m-1} \quad (4) \]
   wherein
     ° R is a hydrophobic organic group which does not undergo hydrolysis in the presence of water,
     ° Q is selected from the group of >NH, >PH, -S- or O-,
     ° Y is a hydroxyl or a hydrolysable group, and
     ° n is from 0 to 5 and m is from 1 to 12,
   and wherein the surface X-O-H groups react with the organosilanes to form X-O-Si bonds.

2. Method according to claim 1, wherein the method at least comprises dispersing the unmodified proppants in at least one organic nonpolar solvent and adding at least one organosilane selected from the group of the organosilanes (1) to (4) to the dispersion.

3. Method according to claim 1, wherein the method at least comprises dissolving or dispersing at least one organosilane selected from the organosilanes (1) and (4) in a non aqueous solvent, pre-condensing the organosilanes by the addition of water to the mixture in an amount of 1 to 10 moles of water per mole of Si and adding unmodified proppants to the mixture comprising pre-condensed organosilanes.

4. Method according to any of claims 1 to 3, wherein the method comprises an additional step of pretreating the unmodified proppants with an aqueous solution of a base, thereby increasing the number of surface X-O-H groups.

5. Method according to any of claims 1 to 4, wherein
R is a hydrocarbon group having from 1 to 30 carbon atoms and wherein the H atoms of the hydrocarbon group may be completely or incompletely substituted by halogen atoms.

Q is >NH, and

Y is selected from the group of hydroxy, methoxy, ethoxy, n-propoxy, iso-propanoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, n-hexoxy, n-octoxy, n-decoxy, n-dodecoxy, n-hexadecoxy, n-octadecoxy, n-cyclohexoxy, vinoxy, phenoxy, benzoxy, phenylethoxy, halide methoxy, F, Cl, Br and I.

6. Method according to any of claims 1 to 4, wherein the groups R are linear or branched alkyl groups R\(^1\) having from 1 to 18 carbon atoms.

7. Method according to any of claims 1 to 4, wherein the groups R are substituted or unsubstituted cycloaliphatic groups R\(^2\) having 5 to 12 carbon atoms.

8. Method according to any of claims 1 to 4, wherein the groups R are linear or branched alkenyl groups R\(^3\) having 2 to 18 carbon atoms.

9. Method according to any of claims 1 to 4, wherein the groups R are substituted or unsubstituted aryl groups R\(^4\) having 5 to 18 carbon atoms.

10. Method according to any of claims 1 to 4, wherein the organosilane has the formula R\(^1\)SiY\(^3\) (1a), wherein the alkyl group R\(^1\) has 4 to 22 carbon atoms.

11. Method according to any of claims 1, 2, and 4, wherein the organosilane has the formula R\(^1\)Si-NH-SiR \(^1\) (3a), wherein the alkyl groups R\(^1\) have 1 to 4 carbon atoms.

12. Method according to any of claims 1 to 4, wherein the organosilane is Y3Si-CnH\(2n\) -C\(_m\)F\(_{2m+1}\) (4).

13. Method according to claim 12, wherein n is 0, 1 or 2 and m is 1, 2, 3, 4, 5 or 6 with the proviso that the sum n + m is from 2 to 16.

14. Proppant having a hydrophobic surface obtainable by a method according to any of claims 1 to 13.
15. Proppant having a omniphobic surface obtainable by a method according to claims 12 or 13.

16. Use of proppants according to claims 14 or 15 for hydraulic fracturing comprising at least the steps of
   ▪ providing an aqueous fracturing fluid comprising at least water and a proppant according to claims 14 or 15,
   ▪ injecting the aqueous fracturing fluid through a wellbore into a subterranean formation at a pressure sufficient to create fractures into the subterranean formation.

17. Use according to claim 16, wherein the fracturing fluid additionally comprises thickening agents.
Figure 1: Schematic diagram of method 1

SUBSTITUTE SHEET (RULE 26)
Figure 2: Schematic diagram of method 2
Figure 3: Wettability tests for examples 4 and 5
INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/05923O

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/80
ADD.

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

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C09

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>Y</td>
<td>US 2013/081812 AI (GREEN JOHN WILLIAM [US] ET AL) 4 April 2013 (2013-04-04) cited in the application claims 1,6; example 2 the whole document</td>
<td>15-17</td>
</tr>
<tr>
<td>X</td>
<td>US 2010/163234 AI (FULLER MICHAEL J [US] ET AL) 1 July 2010 (2010-07-01) cited in the application claims 1,6 the whole document</td>
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Date of the actual completion of the international search: 18 September 2014
Date of mailing of the international search report: 24/09/2014

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