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(54) Title: SHALE HYDRATION INHIBITION AGENT

(57) Abstract: Additives that act to control clay swelling in drilled formations without adversely affecting properties of the drilling fluid are comprised of bis-3-aminopropyl ether amine functionalities, a derivative thereof, or mixtures thereof. The amine is derived by bis-cyanoethylation of terminal hydroxyl functionalities and subsequent hydrogenation of the nitrile end groups to bis-3-aminopropyl primary amines. The backbone comprises a di-ethers or polyethers based on: ethylene oxide (EO), propylene oxide (PO), and all potential isomers of butyl di- or polyethers. Such bis-3-aminopropyl ether amines may include, but are not limited to amines with the following formula: $H_2N-R'-O-(RO)_x-R'-NH_2$ where R' is $(CH_2)_3$; and R is: 1.) C_2H_4 , with x being 2-10, or 2.) branched C_3H_6 , with x being 1-17, or 3.) branched or linear C_4H_8 , with x being 1-15, or 4.) linear C_6H_{12} , with x being 1, or 5.) cyclohexyl-1,4-dimethyl, with x being 1 and mixtures thereof, including, without limitation, Jeffamines (D, M, or XTJ series polyether amines), potassium chloride, choline chloride, and derivatives including partial acid salts of the amines such as those from mineral acids or carboxylic acids with 1-6 carbons.



Shale Hydration Inhibition Agent

BACKGROUND OF THE INVENTION

[0001] A drilling fluid used in the rotary drilling of subterranean wells is expected to perform many functions. For example, the drilling fluid needs to carry cuttings from beneath the drill bit up the annulus, thereby allowing their separation at the surface. At the same time, the drilling fluid is also expected to cool and clean the drill bit, reduce friction between the drill string and the sides of the hole, and maintain stability in the bore hole's uncased sections. The drilling fluid is also expected to form a filter that seals openings in the formations penetrated by the bit so as to reduce the unwanted influx of formation fluids from permeable rocks. In addition, in drilling subterranean wells, formation solids often become dispersed in the drilling fluid. These formation solids typically comprise the cuttings produced by the drill bit's action and the solids produced by the bore hole's instability. The presence of either type of formation solids in the drilling fluid can greatly increase drilling time and costs, especially if the formation solids are clay minerals that swell. The overall increase in bulk volume accompanying clay swelling impedes removal of cuttings from beneath the drill bit, increases friction between the drill string and the sides of the bore hole, inhibits formation of the thin filter that seals formations, and causes loss of circulation or stuck pipe. Accordingly, another function of the drilling fluid is to reduce the adverse effects of formation solids, particularly clay minerals that swell.

[0002] The clay minerals that are encountered in the drilling of subterranean wells are generally crystalline in nature, with a flaky, mica-type structure. The "flakes" of the clay are made up of a number of crystal platelets stacked face-to-face. Each platelet is called a unit layer, and the surfaces of the unit layer are called basal surfaces. A unit layer is composed of multiple sheets. One type of sheet, the octahedral sheet, is composed of either aluminum or magnesium atoms octahedrally coordinated with the oxygen atoms of hydroxyls. Another type of sheet, the tetrahedral sheet, consists of silicon atoms tetrahedrally coordinated with oxygen atoms. Sheets within a unit layer link together by sharing oxygen atoms. When this linking occurs between one octahedral and one tetrahedral sheet, one basal surface consists of exposed oxygen atoms while the other basal surface has exposed hydroxyls. Alternatively, two tetrahedral sheets may bond with one octahedral sheet by sharing oxygen atoms. The resulting structure, known as the Hoffman structure, has an octahedral sheet that is sandwiched between the two tetrahedral sheets. As a result, both basal surfaces in a Hoffman structure are composed of exposed oxygen atoms. The individual unit layers of the clay are stacked together face-to-face, and are held in place by weak attractive forces. The distance between corresponding planes in adjacent unit layers is called the c-spacing.

[0003] In clay mineral crystals, atoms having different valences commonly will be positioned within the sheets of the structure to create a negative potential at the crystal surface. When the clay crystal is suspended in water, a cation may be adsorbed on the surface, and these absorbed cations, often called exchangeable cations, may chemically trade places with other cations. In

addition, ions may also be adsorbed on the clay crystal edges and exchange with other ions in the water.

[0004] The type of substitutions occurring within the clay crystal structure and the exchangeable cations adsorbed on the crystal surface greatly affect clay swelling. Clay swelling is a phenomenon in which water molecules surround a clay crystal structure and position themselves to increase the structure's c-spacing, which causes an increase in the volume of the clay. Two types of swelling may occur, either surface hydration or osmotic. Only certain clays, such as sodium montmorillonite, exhibit osmotic swelling, whereas all clays exhibit surface hydration swelling.

[0005] Surface hydration swelling involves the hydrogen bonding of water molecules to the oxygen atoms exposed on the crystal surface, which results in layers of water molecules aligning to form a quasi-crystalline structure between the unit, thereby increasing the c-spacing. In osmotic swelling, if the concentration of cations between unit layers in a clay mineral is higher than the cation concentration in the surrounding water, water will be osmotically drawn between the unit layers, thereby increasing the c-spacing. Osmotic swelling typically causes the clay to swell more than surface hydration.

[0006] Exchangeable cations found in clay minerals are reported to have a significant impact on the amount of swelling that takes place. The exchangeable cations compete with water molecules for the available reactive sites in the clay structure. Generally, cations with high valences are more strongly adsorbed than cations with low valences. Thus, clays with low valence exchangeable cations will swell more than clays whose exchangeable cations have high valences.

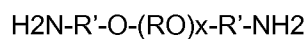
[0007] In the North Sea and the United States Gulf Coast, drillers commonly encounter argillaceous sediments in which the predominant clay mineral is sodium montmorillonite (commonly called "gumbo clay"). Sodium cations are predominately the exchangeable cations in gumbo clay. Because the sodium cation has a low positive valence (+1 valence) it easily disperses into water. Consequently, gumbo clay is notorious for its swelling. Thus, given the frequency in which gumbo clay is encountered in drilling subterranean wells, the development of a substance and method for reducing clay swelling is of primary importance in the drilling industry.

[0008] One commonly employed method to reduce clay swelling is the addition of salts to the drilling fluids. However, salts flocculate the clays, which causes both high fluid losses and an almost complete loss of thixotropy. Further, increasing salinity often decreases the functional characteristics of drilling fluid.

[0009] Accordingly, there is a long felt need for a drilling fluid additive that acts to control clay swelling in drilled formations without adversely affecting the properties of drilling fluids; a drilling fluid that contains such drilling fluid additive; and a method of reducing clay swelling in a drilled formation. The present invention is directed towards meeting these needs.

BRIEF SUMMARY OF THE INVENTION

[0010] In one embodiment, the present invention is directed towards a drilling fluid for drilling wells through formations containing shale clay that swells in presence of water but is not limited to such use. The clay hydration inhibition agent preferably comprises bis-3-aminopropyl ether amine functionalities, a derivative thereof, or mixtures thereof. The amine is derived by bis-cyanoethylation of terminal hydroxyl functionalities and subsequent hydrogenation of the nitrile end groups to bis-3-aminopropyl primary amines. The backbone comprises a di-ethers or polyethers based on: ethylene oxide (EO), propylene oxide (PO), and all potential isomers of butyl di- or polyethers. Such bis-3-aminopropyl ether amines may include, but are not limited to amines with the following formula:



where R' is (CH₂)₃; and R is:

- 1.) C₂H₄, with x being 2-10, or
- 2.) branched C₃H₆, with x being 1-17, or
- 3.) branched or linear C₄H₈, with x being 1-15, or
- 4.) linear C₆H₁₂, with x being 1, or
- 5.) cyclohexyl-1,4-dimethyl, with x being 1

and mixtures thereof, including, without limitation, Jeffamines (D, M, or XTJ series polyether amines), potassium chloride, choline chloride, and derivatives including partial acid salts of the amines such as those from mineral acids or carboxylic acids with 1-6 carbons.

[0011] As a class of molecules, by neither particular mention nor generalized structure, these bis-3-aminopropyl ether amines have not been previously identified or claimed to function in controlling such clay hydration/swelling.

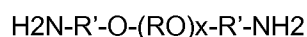
[0012] Prior art indicates the use of directly aminated polyethers based on ethylene oxide and/or propylene oxide (Jeffamine products, Huntsman Chemical) as being useful in the inhibition of shale hydration / swelling in drilling operations (US Pats. 6483821, 6609578, 7012043). These mono-, di-, and triamines and other amines have been identified and employed for this purpose. Along with these 2-aminopropyl or 2-aminoethyl moieties, it is notable that only one specific bis-3-aminopropyl ether amine, based on ethylene glycol, has been claimed as being useful in this application.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In one embodiment, the present invention is directed towards a drilling fluid for drilling wells through formations containing clay that swells in the presence of water. Preferably, the drilling fluid comprises a weight material, a clay hydration inhibition agent, and an aqueous continuous phase. The drilling fluids of the present invention may also include additional components, such as fluid loss control agents, bridging agents, lubricants, anti-bit balling agents, corrosion inhibition agents, surfactants, suspending agents, and the like which are known to those skilled in the art.

[0014] The weight material in the drilling fluids of the present inventions increases the density of the fluid, which helps prevent kick-backs and blow-outs. The amount of weight material in the drilling fluid composition will depend largely on the nature of the formation being drilled. The weight material component of the drilling fluids of the present invention may be generally selected from any type of weighting materials, including, without limitation, solids, those in particulate form, those suspended in solution, those dissolved in the aqueous phase as part of the preparation process, or those added during drilling. It is preferred that the weight material be selected from the group including barite, hematite, iron oxide, calcium carbonate, magnesium carbonate, organic and inorganic salts, and mixtures and combinations of these compounds and similar such weight materials that are commonly used in the art.

[0015] The clay hydration inhibition agent should be present in sufficient concentration to reduce surface hydration swelling and/or osmotic swelling of the clay. The exact amount of the clay hydration inhibition agent present in a particular drilling fluid formulation can be determined by a trial and error method of testing the combination of drilling fluid and clay formation encountered. Generally, however, the clay hydration inhibition agent should be present in a concentration from about 1 to about 18 pounds per barrel (lbs/bbl or ppb) and more preferably in a concentration from about 2 to about 12 pounds per barrel of drilling fluid. Preferably, the clay hydration inhibition agent comprises a polyether amine, a polyether amine derivative, or mixtures thereof. The clay hydration inhibition agents of the present invention comprise a bis-3-aminopropyl ether amine functionalities, a derivative thereof, or mixtures thereof. The amine is derived by bis-cyanoethylation of terminal hydroxyl functionalities and subsequent hydrogenation of the nitrile end groups to bis-3-aminopropyl primary amines (see "Cyanoethylation", Kirk-Othmer Encycl. Chem. Technol. 3rd Ed. 1979, Vol. 7, p. 370). The backbone comprised of a di-ethers or polyethers based on: ethylene oxide (EO), propylene oxide (PO), and all potential isomers of butyl di- or polyethers. Such bis-3-aminopropyl ether amines may include, but are not limited to amines with the following formula:



where R' is (CH₂)₃; and R is:

- 1.) C₂H₄, with x being 2-10, or
- 2.) branched C₃H₆, with x being 1-17, or
- 3.) branched or linear C₄H₈, with x being 1-15, or
- 4.) linear C₆H₁₂, with x being 1, or
- 5.) cyclohexyl-1,4-dimethyl, with x being 1

Mixtures of the polyether amines and polyether amine derivatives may include any combination of the polyether amines and polyether amine derivatives disclosed herein but also may mixed with other amines of such purpose.

[0016] The aqueous based continuous phase component of the drilling fluid of the present invention may generally be any water based fluid phase that is suitable for use in a drilling fluid and is compatible with the clay hydration inhibition agents disclosed herein. Preferably, the aqueous based continuous phase is selected from the group comprising fresh water, sea water, brine,

mixtures of water and water soluble organic compounds, or mixtures thereof. The amount of the aqueous based continuous phase component in the drilling fluid of the present invention will vary, depending on the drilling application and the nature of the other components in the drilling fluid. Typically, the amount of the aqueous based continuous phase may range from nearly 100% of the drilling fluid to less than 30% of the drilling fluid by volume.

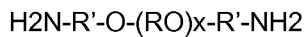
[0017] Additionally, an acid maybe added to the drilling fluid compositions of the present invention to neutralize the drilling fluid for handling purposes. Any suitable acid may be used. Preferably, the acid should not form a salt that is not soluble. More preferably, the acid comprises hydrochloric acid. Preferably, the drilling fluid is neutralized to a pH of approximately pH 9.

[0018] In addition, the drilling fluids of the present invention may further comprise gelling materials, thinners, and fluid loss control agents. Typical gelling materials used in aqueous based drilling fluids include, but are not limited to, bentonite, sepiolite clay, attapulgite clay, anionic high-molecular weight polymer and biopolymers. Typical thinners include, but are not limited to, lignosulfonates modified lignosulfonates, polyphosphates, tannins, and low molecular weight polyacrylates. Thinners are added to a drilling fluid to reduce flow resistance, control gelation tendencies, reduce filtration and filter cake thickness, counteract the effects of salts, minimize the effects of water on the formations drilled, emulsify the oil in water, and stabilize the mud properties at elevated temperatures. Suitable fluid control agents include, but are not limited to, synthetic organic polymers, biopolymers, and mixtures thereof. The fluid loss control agents may also comprise modified lignite, polymers, and modified starches and celluloses. Ideally, the additives should be selected to have low toxicity and to be compatible with common drilling fluid additives, such as polyanionic carboxymethylcellulose (PAC or CMC), polyacrylates, partially-hydrolyzed polyacrylamides (PHPA), lignosulfonates, xanthan gum, mixtures of these and the like.

[0019] The drilling fluids of the present invention may further contain an encapsulating agent. Encapsulating agents help improve the removal of cuttings with less dispersion of the cuttings into the drilling fluids. The encapsulating agents may be anionic, cationic or non-ionic in nature.

[0020] Other drilling fluid additives may also be added to the drilling fluids of the present invention, including products such as lubricants, penetration rate enhancers, defoamers, corrosion inhibitors, loss circulation products, and other similar products known to those skilled in the art.

[0021] In another embodiment, the present invention is directed towards clay hydration inhibition agents that inhibit the swelling of clay that may be encountered during the drilling of wells. The clay hydration inhibition agents of the present invention preferably comprises bis-3-aminopropyl ether amine functionalities, a derivative thereof, or mixtures thereof. The amine is derived by bis-cyanoethylation of terminal hydroxyl functionalities and subsequent hydrogenation of the nitrile end groups to bis-3-aminopropyl primary amines. The backbone comprises a di-ethers or polyethers based on: ethylene oxide (EO), propylene oxide (PO), and all potential isomers of butyl di- or polyethers. Such bis-3-aminopropyl ether amines may include, but are not limited to amines with the following formula:



where R' is (CH₂)₃; and R is:

- 1.) C₂H₄, with x being 2-10, or
- 2.) branched C₃H₆, with x being 1-17, or
- 5 3.) branched or linear C₄H₈, with x being 1-15, or
- 4.) linear C₆H₁₂, with x being 1, or
- 5.) cyclohexyl-1,4-dimethyl, with x being 1

and mixtures thereof, including, without limitation, Jeffamines (D, M, or XTJ series polyether amines), potassium chloride, choline chloride, and derivatives including partial acid salts of the amines such as those from mineral acids or carboxylic acids with 1-6 carbons.

[0022] Preferably, the mixtures of the polyether amines and polyether amine derivatives contain less than about 50% of the polyether amine derivative component.

[0023] Additionally, an acid maybe added to the clay hydration inhibition agents of the present invention to neutralize the clay hydration inhibition agent for handling purposes. Any suitable acid may be used. Preferably, the acid should not form a salt that is not soluble. More preferably, the acid comprises hydrochloric acid. Preferably, the drilling fluid is neutralized to a pH of approximately pH 9.

[0024] In another embodiment, the present invention includes a method of reducing the swelling of clay in a well, involving circulating in the well a drilling fluid formulated in accordance with the present disclosure. Preferably, the drilling fluid comprises a weight material, a clay hydration inhibition agent, and an aqueous continuous phase. The drilling fluid may also comprise additional components, such as fluid loss control agents, bridging agents, lubricants, anti-bit balling agents, corrosion inhibition agents, surfactants, suspending agents, and the like which are known to those skilled in the art.

[0025] The weight material may be generally selected from any type of weighting materials, including, without limitation, solids, those in particulate form, those suspended in solution, those dissolved in the aqueous phase as part of the preparation process, or those added afterward during drilling. It is preferred that the weight material be selected from the group including barite, hematite, iron oxide, calcium carbonate, magnesium carbonate, organic and inorganic salts, and mixtures and combinations of these compounds and similar such weight materials that are commonly used in the art. The amount of weight material in the drilling fluid composition will depend largely on the nature of the formation being drilled.

[0026] The clay hydration inhibition agent should be present in sufficient concentration to reduce surface hydration swelling and/or osmotic swelling of the clay. The exact amount of the clay hydration inhibition agent present in a particular drilling fluid formulation can be determined by a trial and error method of testing the combination of drilling fluid and clay formation encountered. Generally, however, the clay hydration inhibition agent should be present in a concentration from about 1 to about 18 pounds per barrel (lbs/bbl or ppb) and more preferably in a concentration from

about 2 to about 12 pounds per barrel of drilling fluid. Preferably, the clay hydration inhibition agent comprises bis-3-aminopropyl ether amine functionalities, a derivative thereof, or mixtures thereof. The amine is derived by bis-cyanoethylation of terminal hydroxyl functionalities and subsequent hydrogenation of the nitrile end groups to bis-3-aminopropyl primary amines. The backbone
 5 comprises a di-ethers or polyethers based on: ethylene oxide (EO), propylene oxide (PO), and all potential isomers of butyl di- or polyethers. Such bis-3-aminopropyl ether amines may include, but are not limited to amines with the following formula:



where R' is (CH₂)₃; and R is:

- 10 1.) C₂H₄, with x being 2-10, or
- 2.) branched C₃H₆, with x being 1-17, or
- 3.) branched or linear C₄H₈, with x being 1-15, or
- 4.) linear C₆H₁₂, with x being 1, or
- 5.) cyclohexyl-1,4-dimethyl, with x being 1

15 and mixtures thereof, including, without limitation, Jeffamines (D, M, or XTJ series polyether amines), potassium chloride, choline chloride, and derivatives including partial acid salts of the amines such as those from mineral acids or carboxylic acids with 1-6 carbons.

[0027] Preferably, the mixtures of the polyether amines and polyether amine derivatives contain less than about 50% of the polyether amine derivative component.

20 **[0028]** The aqueous based continuous may generally be any water based fluid phase that is suitable for use in a drilling fluid and is compatible with the clay hydration inhibition agents disclosed herein. Preferably, the aqueous based continuous phase is selected from the group comprising fresh water, sea water, brine, mixtures of water and water soluble organic compounds, or mixtures thereof. The amount of the aqueous based continuous phase component in the drilling
 25 fluid of the present invention will vary, depending on the drilling application and the nature of the other components in the drilling fluid. Typically, the amount of the aqueous based continuous phase may range from nearly 100% of the drilling fluid to less than 30% of the drilling fluid by volume.

30 **[0029]** Additionally, the drilling fluid composition may further comprise an acid to neutralize the drilling fluid for handling purposes. Any suitable acid may be used. Preferably, the acid should not form a salt that is not soluble. More preferably, the acid comprises hydrochloric acid. Preferably, the drilling fluid is neutralized to a pH of approximately pH 9.

[0030] In addition, the drilling fluid may further comprise gelling materials, thinners, and fluid loss control agents. The gelling materials may include, but are not limited to, bentonite sepiolite clay,
 35 attapulgite clay, anionic high-molecular weight polymer and biopolymers. The thinners may include but are not limited to, lignosulfonates, modified lignosulfonates, polyphosphates, tannins, and low molecular weight polyacrylates. The fluid control agents may include, but are not limited to,

synthetic organic polymers, biopolymers, and mixtures thereof. The fluid loss control agents may also include modified lignite, polymers, and modified starches and celluloses.

[0031] Other drilling fluid additives may also be added to the drilling fluids, including products such as encapsulating agents, lubricants, penetration rate enhancers, defoamers, corrosion inhibitors, loss circulation products, and other similar products known to those skilled in the art.

[0032] In addition to the inhibition of clay hydration by the clay hydration inhibition agent, other beneficial properties are likely to be achieved. In particular it is expected that the clay hydration inhibition agents of the present invention are compatible with other drilling fluid components, are tolerant to contaminants, show temperature stability, and exhibit low toxicity. Therefore, it is expected that the clay hydration inhibition agents of the present invention may have broad application both in land based drilling operations, as well as offshore drilling operations.

[0033] It is understood that variations may be made in the foregoing without departing from the scope of the invention.

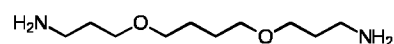
EXAMPLES

[0034] The following example is illustrative of the present invention, and is not intended to limit the scope of the invention in any way. Those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the invention.

[0035] The following examples were compared to commonly used competitive shale swell inhibition materials, potassium chloride (KCl), choline chloride, and Huntsman's Jeffamine D230.

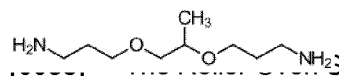
[0036] Example Compound 1

NDPA-12 as produced by Air Products



[0037] Example Compound 2

DPA-PG, also produced by Air Products



Shale Stability test (API Recommended Practice 13I Section 23) was run using shale (Pierre II shale) ground to a particle size less than 4 mm (5 mesh) and larger than 2mm (10 mesh). The particles were split equal into 20 gram samples. Each weighed sample was placed in a glass bottle along with 350 milliliters of the test fluid and hot rolled in a roller oven at 160°F for 16 hours. The samples were then screened through 35 mesh screen (0.5 mm) and washed with deionized water prior to drying and reweighing.

[0039] Table 1 presents data from the Roller Oven Shale Stability test. The higher the mass fraction of the shale that is recovered indicates improved shale inhibition.

TABLE 1

% Inhibitor in Water	Mass Fraction of Shale Recovered				
	0.50%	0.75	1.0%	1.25%	1.50%
NDPA-12	82	82	82	81	81
DPA-PG	83	82	80	81	79
KCl	7	10	12	11	14
Jeffamine D-230	75	72	71	73	88
Choline Chloride	59	57	55	64	63

[0040] The tendency for a shale to adsorb fluid from a water-based fluid can lead to a swelling of the shales which can translate to decreased wellbore size and wellbore instability issues as well as swollen cuttings which tend to be more adhesive in nature and can, in turn, lead to bit balling and poor rate of penetration. The amount of fluid adsorbed by shale over time can be determined in the laboratory using the Linear Swellmeter. In this test the shale to be tested is ground into a powder, then compressed into a sized shale pellet which is placed between a metal plate and a linear transducer. The pellet is immersed in the test fluid and the change in length of the pellet is measured over time by the transducer. Both the total change in length over a given time period and the constant rate of change can be determined. Testing was determined using a Bariod Linear Swellmeter Model 2000.

[0041] Table 2 presents data from the Linear Swellmeter, thus illustrating the shale inhibition effects of the present invention in comparison to commonly used shale inhibitors. The longer the time to reach maximum swell and the lower the percentage of maximum swell is advantageous to the invention.

TABLE 2

% Inhibitor in Water	Time, (h)					Swell, (%)				
	0.50 %	0.75 %	1 %	1.25 %	1.50 %	0.50 %	0.75 %	1 %	1.25 %	1.50 %
NDPA-12	25	17	21	25	25	18	17	17	16	16
DPA-PG	25	25	25	20	19	25	20	20	20	20
KCl	16	12	12	15	14	19	16	16	16	16
Jeffamine D-230	27	25	25	25	25	24	23	23	22	22
Choline Chloride	14	17	15	17	20	21	16	15	16	17

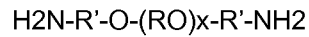
[0042] Although illustrative embodiments have been shown and described, a wide range of modification, changes and substitution is contemplated in the foregoing disclosure. In some instances, some features of the disclosed embodiments may be employed without a corresponding use of the other features.

CLAIMS

1. A drilling fluid for use in drilling wells through a formation containing a clay that swells in the presence of water, the drilling fluid comprising:
 - (a) an aqueous based continuous phase;
 - 5 (b) a weight material; and
 - (c) a clay hydration inhibition agent that comprises a bis-3-aminopropyl amine with the following formula:

$$\text{H}_2\text{N}-\text{R}'-\text{O}-(\text{RO})_x-\text{R}'-\text{NH}_2$$
 Wherein R' is $(\text{CH}_2)_3$ and R is:
 - 10 i.) C_2H_4 , with x being 2-10, or
 - ii.) branched C_3H_6 , with x being 1-17, or
 - iii.) branched or linear C_4H_8 , with x being 1-15, or
 - iv.) linear C_6H_{12} , with x being 1, or
 - v.) cyclohexyl-1,4-dimethyl, with x being 1
 - 15 and optionally a partial salt thereof.
2. The drilling fluid of claim 1, wherein in the amine i.) x is 2-4
3. The drilling fluid of claim 1, wherein in the amine ii.) x is 1-3
- 20 4. The drilling fluid of claim 1, wherein in the amine iii.) is linear and x is 1
5. The drilling fluid of claim 1, wherein in the amine is partially neutralized with HCl to a pH of approximately 9.
- 25 6. The drilling fluid of claim 1, where the aqueous based continuous phase is selected from the group consisting of fresh water, sea water, brine, mixtures of water and water soluble organic compounds, and mixtures thereof.
- 30 7. The drilling fluid of claim 1, wherein the weight material is selected from the group consisting of barite, hematite, iron oxide, calcium carbonate, magnesium carbonate, magnesium organic and inorganic salts, calcium chloride, calcium bromide, magnesium chloride, zinc halides, and combinations thereof.
- 35 8. A method of reducing the swelling of clay encountered during the drilling of a subterranean well, the method comprising the step of circulating in the subterranean well a drilling fluid comprising:
 - (a) an aqueous based continuous phase;
 - (b) a weight material; and

- (c) a clay hydration inhibition agent that comprises a bis-3-aminopropyl amine with the following formula:



Wherein R' is (CH₂)₃ and R is:

- 5 i.) C₂H₄, with x being 2-10, or
 ii.) branched C₃H₆, with x being 1-17, or
 iii.) branched or linear C₄H₈, with x being 1-15, or
 iv.) linear C₆H₁₂, with x being 1, or
 v.) cyclohexyl-1,4-dimethyl, with x being 1
 10 and optionally a partial salt thereof.

9. The drilling fluid of claim 8, wherein in the amine i.) x is 2-4
10. The drilling fluid of claim 8, wherein in the amine ii.) x is 1-3
 15
11. The drilling fluid of claim 8, wherein in the amine iii.) is linear and x is 1
12. The drilling fluid of claim 8, wherein in the amine is partially neutralized with HCl to a pH of approximately 9.
 20
13. The drilling fluid of claim 8, where the aqueous based continuous phase is selected from the group consisting of fresh water, sea water, brine, mixtures of water and water soluble organic compounds, and mixtures thereof.
- 25 14. The drilling fluid of claim 8, wherein the weight material is selected from the group consisting of barite, hematite, iron oxide, calcium carbonate, magnesium carbonate, magnesium organic and inorganic salts, calcium chloride, calcium bromide, magnesium chloride, zinc halides, and combinations thereof.
- 30 15. A clay hydration inhibition agent that comprises a bis-3-aminopropyl amine with the following formula:

$$\text{H}_2\text{N}-\text{R}'-\text{O}-(\text{RO})_x-\text{R}'-\text{NH}_2$$

 Wherein R' is (CH₂)₃ and R is:
 35 i.) C₂H₄, with x being 2-10, or
 ii.) branched C₃H₆, with x being 1-17, or
 iii.) branched or linear C₄H₈, with x being 1-15, or
 iv.) linear C₆H₁₂, with x being 1, or
 v.) cyclohexyl-1,4-dimethyl, with x being 1
 40 and optionally a partial salt thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/080892

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/035 C09K8/06
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)
C09K

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/148892 A1 (KLEIN HOWARD P [US] ET AL) 7 August 2003 (2003-08-07) the whole document -----	1-15
A	WO 2006/096731 A1 (MI LLC [US]; BALLARD DAVID [GB]) 14 September 2006 (2006-09-14) the whole document -----	1-15
A	CN 105 778 076 A (PETROCHINA CO LTD) 20 July 2016 (2016-07-20) the whole document -----	1-15
A	WO 2014/004193 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 3 January 2014 (2014-01-03) the whole document -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

23 January 2018

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/080892

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