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(54) Title: METHOD OF STABILIZING CLAY USING A POLYIMIDAZOLIUM COMPOUND

(57) Abstract: The present invention relates to a method of inhibiting the swelling of clay in subterranean formations by introducing a carrier fluid into the formation, wherein the carrier fluid comprises at least one clay stabilizer which is a cationic polymer comprising imidazolium groups having a weight average molecular weight M_w of about 1,000 g/mol to about 20,000 g/mol.

METHOD OF STABILIZING CLAY USING A POLYIMIDAZOLIUM COMPOUND

The present invention relates to a method of inhibiting the swelling of clay in subterranean formations by introducing a carrier fluid into the formation, wherein the carrier fluid comprises at least one clay stabilizer which is a cationic polymer comprising imidazolium groups having a weight average molecular weight M_w of about 1,000 g/mol to about 20,000 g/mol.

Subterranean oil-bearing formations often comprise clays. The presence of such clays may give rise to problems when oil is produced from such formations and the clays come into contact with aqueous fluids injected into the formation such as stimulation fluids or fluids for enhanced oil recovery and/or connate waters because the clays can swell thereby reducing the permeability of the formation.

It is known in the art to use additives which inhibit or at least minimize swelling or disintegration and migration of clay. For example, such additives may be added to the treatment fluid and/or the formation may be pre-flushed with an aqueous fluid which comprises such additive(s).

Suitable additives include inorganic salts, in particular potassium chloride. It is assumed that K^+ ions exchange against Na^+ ions present in the clays thus yielding modified clays which are less sensitive to swelling in aqueous fluids.

It is also known in the art to use monomeric or polymeric organic compounds for clay inhibition, such as for example choline chloride or choline formate.

US 8,084,402 B2 discloses a method of inhibiting swelling of clay particulates by injecting a well treatment formulation which comprises imidazolium cations derived from imidazole or substituted imidazole and various anions.

US 2012/0103614 A1 discloses a drilling fluid which comprises imidazolium cations.

US 6,350,721 B1 discloses a fluid for matrix acidizing which comprises imidazolium and/or pyridinium salts.

US 4,158,521 discloses a method for stabilization of an subterranean formation comprising clay particles using a copolymer of epichlorhydrin and dimethylamine.

US 4,447,342 discloses to use cationic polymers for clay stabilization, for example poly(1,5-dimethyl-1,5-diaza-undecamethylene methobromide), poly(dimethylamine-co-epichlorhydrine), Poly(diallyldimethylammonium chloride) or poly(methacrylamido-4,8-diaza-4,4,8,8-tetramethyl-6-hydroxynonamethylene methochloride).

US 2004/0045712 A1 discloses polymers of a dialkyl aminoalkyl methacrylate which can optionally be quaternized with an alkyl halide for clay inhibition.

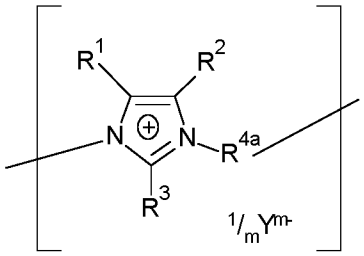
US 2005/0215439 A1 discloses a composition for clay stabilization comprising poly(dimethylamino(meth)acrylate quaternary salt) having a molecular weight of 1,000 g/mol to 100,000 g/mole.

Although already a number of clay inhibitors are known in the art there is still a need for improvements in particular with respect to permanent clay inhibition. Many inhibitors have only a temporary effect. Once the clay is no longer in contact with the solution comprising the inhibitors the effect of the inhibitors decreases. There is need for improved inhibitors having a permanent effect, i.e. the effect of the inhibitors should be maintained for a long time even if US 6,146,770 B1 discloses cationic polymers comprising imidazolium groups in which the nitrogen atoms of the imidazolium groups are linked together with spacer groups such as polyalkylene groups. The polymers are available by reaction of compounds comprising two imidazole groups with dibromo compounds. It is suggested to use such cationic polymers as protective agent for keratin fibres, e.g. in cosmetic compositions, hair dyeing compositions or bleaching compositions. It has not been suggested to use such polymers for oilfield applications.

US 2011/0263810 A1 discloses cationic polymers comprising imidazolium groups in which the nitrogen atoms of the imidazolium groups are linked together with spacer groups such as polyalkylene groups which are available by reaction of an α-dicarbonyl compound, an aldehyde, at least one amino compound having at least two primary amino groups, and a protic acid. The number average molecular weight M_n of the polyimidazolium polymers may be from 500 g/mol to 500,000 g/mol, in particular 500 g/mol to 50,000 g/mol. It is suggested to use such cationic polymers as dispersants. It has not been suggested to use such polymers for oilfield applications.

It was an object of the present invention to provide a method for long-term inhibition of the swelling of clays in subterranean formations.

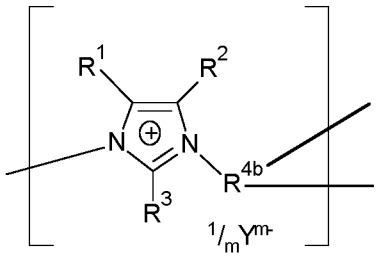
Correspondingly, a method of inhibiting the swelling of clay in subterranean formations has been found which comprises the step of introducing an aqueous carrier fluid comprising at least one clay inhibitor (shale inhibitor) into the formation, wherein at least one of the clay inhibitors is a cationic polymer comprising repeating units (I) of formula (Ia)



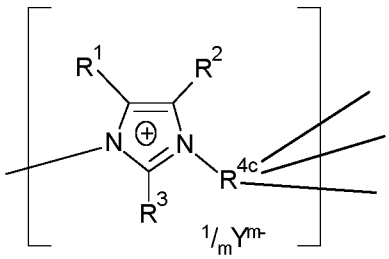
(Ia)

,

and optionally repeating units of formulae (Ib) and/or (Ic)



(Ib)



(Ic)

,

wherein

R^1, R^2, and R^3 are each, independently of one another, H or a saturated or unsaturated, branched or unbranched, aliphatic and/or aromatic hydrocarbon moiety having from 1 to 20 carbon atoms which optionally may be substituted with functional groups,

R^{4a}, R^{4b}, R^{4c} are each, independently from one another, organic groups comprising 2 to 50 carbon atoms, wherein the organic groups R^{4a}, R^{4b}, and R^{4c} may optionally comprise functional groups and/or non-neighboring carbon atoms of the organic group may be substituted by heteroatoms,

Y^{m-} are each, independently of one another, anionic counter ions, wherein m is an integer from 1 to 4,

and wherein the cationic polymer has a weight average molecular weight M_w of about 1,000 g/mol to about 20,000 g/mol.

Cationic polymers

For the method of inhibiting the swelling of clay according to the present invention cationic polymers comprising imidazolium groups are used. Such polymers are sometimes also termed as polymeric imidazolium salts.

In the cationic polymers imidazolium cations are linked together via their N-atoms by divalent organic groups R^{4a} to form a linear polymer chain. Cationic polymers comprising also 3- or 4-valent linking groups yield branched polymers. The polymers may comprise the same or different groups R^{4a} and optionally the same and different groups R^{4b} and/or R^{4c}. In one embodiment the polymers comprise only the repeating unit of formula (Ia).

In formulas (Ia), (Ib) and (Ic) R^1, R^2, and R^3 are each, independently of one another, an H atom or a saturated or unsaturated, branched or unbranched, aliphatic and/or aromatic hydrocarbon moiety having from 1 to 20 carbon atoms. The hydrocarbon moieties may be unsubstituted or may comprise additional functional groups. In one embodiment of the invention, R^1, R^2 and R^3 are hydrogen or saturated, aliphatic hydrocarbon moieties having from 1 to 20, preferably 1 to 6 carbon atoms. In a preferred embodiment, R^1, R^2 and R^3 are H.

The groups R^{4a}, R^{4b}, and R^{4c} are organic groups each. The term “organic groups” means in principally known manner that the group at least comprises carbon atoms and hydrogen atoms. Preferably, the organic groups R^{4a}, R^{4b}, and R^{4c} comprise, independently of one another, 2 to 50 carbon atoms, in particular 4 to 50, more preferably 4 to 40 and particularly 4 to 20 carbon atoms. The groups may be aliphatic and/or aromatic groups, preferably aliphatic groups.

Besides carbon and hydrogen the organic groups R^{4a}, R^{4b}, and R^{4c} may comprise functional groups and/or non-neighboring carbon atoms may be substituted by heteroatoms, in particular O- and/or N atoms. Examples of functional groups comprise hydroxyl groups, ether groups, ester groups, amide groups, aromatic heterocycles, keto groups, aldehyde groups, primary or secondary amino groups, imino groups, thioether groups, halide groups or acid groups such as carboxylic acid groups, phosphonic acid groups or phosphoric acid groups.

In one embodiment, the linking groups R^{4a}, R^{4b}, and R^{4c} may comprise ether groups or secondary or tertiary amino groups and apart from these no further functional groups.

In one preferred embodiment, R^{4a}, R^{4b}, and R^{4c} are pure hydrocarbon moieties and do not comprise any functional groups. The hydrocarbon moieties may be aliphatic or aromatic or may comprise both aromatic and aliphatic groups. Preferably, R^{4a}, R^{4b}, and R^{4c} are aliphatic moieties.

The bivalent linking groups R^{4a} preferably are aliphatic hydrocarbon moieties, preferably linear aliphatic hydrocarbon moieties comprising 2 to 50 carbon atoms, preferably 3 to 40 and particularly 4 to 20 carbon atoms which may optionally be further substituted. If the groups are substituted they preferably comprise ether groups, secondary or tertiary amino groups, or carboxylic acid groups and apart from these no further functional groups. Preferably, the groups R^{4a} are unsubstituted.

According to a preferred embodiment, the bivalent linking group R^{4a} is an aliphatic hydrocarbon moiety, preferably a linear aliphatic hydrocarbon moiety comprising 2 to 50 carbon atoms, preferably 3 to 40 and particularly 4 to 20 carbon atoms, which aliphatic hydrocarbon moiety is optionally substituted with at least one carboxylic acid group, preferably in 2-position (in case of more than two carbon atoms).

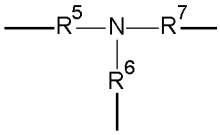
According to a further embodiment, the bivalent linking group R^{4a} is a C_4 to C_{12} alkylene group or a C_5 alkylene group which is substituted with a carboxylic acid group. Examples of preferred bivalent linking groups R^{4a} comprise C_2-C_{20} alkylene groups, preferably C_4-C_{12} alkylene groups optionally substituted with at least one carboxylic acid group such as a 1,4-butylene, 1,5-pentylene, 1,6-hexylene, or 1,12-dodecylene or 1,4-butylene, 1,5-pentylene, 1,6-hexylene, 1,12-dodecylene which is substituted with a carboxyl group, in particular in 2-position.

According to a further embodiment, the bivalent linking group R^{4a} is a group of the general formula $-(CH_2)_y-X-(CH_2)_{y'}-$ (IIa), wherein X is a group selected form arylene groups, such as a 1,4-phenylene group, cycloalkylene groups, such as a 1,4-cyclohexylene group, and y and y' independently of each other are 1, 2, 3 or 4.

According to a further embodiment, the bivalent linking group R^{4a} is a polyether group $-(-CH_2-CH_2O-)_z-CH_2CH_2-$, wherein z is from 1 to 49, preferably from 2 to 40.

Trivalent linking groups R^{4b} preferably are aliphatic hydrocarbon moieties, comprising 3 to 40 and particularly 4 to 20 carbon atoms which may optionally be further substituted. If the groups are substituted they preferably comprise at most ether groups, secondary or tertiary amino groups, or carboxylic acid groups and apart from these no further functional groups. It is self-evident that R^{4b} comprises at least one branching atom. Such branching atom may be a carbon atom but it may also be a N-atom.

Examples of preferred trivalent linking groups R^{4b} comprise groups of the formula (II)

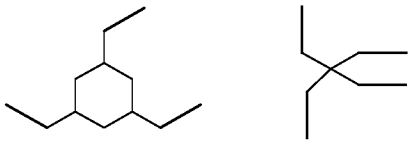


(II)

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wherein R^5, R^6 and R^7 are each, independently of one another, C_1-C_{10} alkylene groups, preferably a C_2-C_6-alkylene groups. In one embodiment R^5, R^6 and R^7 have the same meaning and may be an ethylene group $-CH_2CH_2-$ each.

Further examples of trivalent linking groups R^{4b} comprise the groups



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Tetravalent linking groups R^{4c} preferably are aliphatic hydrocarbon moieties comprising 4 to 40 and particularly 4 to 20 carbon atoms which may optionally be further substituted. If the groups are substituted they preferably comprise at most ether groups, secondary or tertiary amino groups, or carboxylic acid groups and apart from these no further functional groups. It is self-evident that R^{4c} comprises at least one branching atom. Such branching atom may be a carbon atom but it may also be a N-atom.

Examples of preferred tetravalent linking groups R^{4c} comprise the groups



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The cationic polymers comprising imidazolium groups may optionally comprise besides the groups (Ia), and optionally (Ib), or (Ic) other repeating units. Introducing other repeating units may be performed by the skilled artisan in order to fine tune the properties of the cationic polymer. In general, the amount of repeating units (I), selected from (Ia), (Ib), and (Ic) is at least 80 mol %, relating to the total amount of all repeating units, preferably at least 90 mol % and particularly 95 mol % repeating units of formula (Ia). Repeating units (Ib), and/or (Ic) may be present in amounts up to 20 mol %, up to 10 mol % or up to 5 mol %, in particular in amounts of 0.1 to 20 mol %, preferably 0.2 to 10 mol % and in particular 0.5 to 5 mol %, based on the amount of repeating units (Ia). Particularly preferred is a polymer comprising only repeating units (Ia). It goes without saying for the skilled artisan that the polymer also comprises terminal groups (amine groups) which have a structure different from that of the repeating units.

The cationic polymers comprising imidazolium groups furthermore comprise negatively charged counter ions. Such counter ions may be separate ions Y^{m-}, wherein m is a positive integer. In a preferred embodiment, m is an integer from 1 to 4, particularly preferably 1 or 2. In a particular embodiment, m is 1. The number of counter ions is $^1/_m$ per imidazolium group. If the linking groups R^{4a}, R^{4b}, and R^{4c} comprise anionic groups or groups which can be converted into anionic groups, e.g. carboxylic acid groups, a separate counter ion may not be necessary. In such a case the polymer comprising imidazolium groups is amphoteric, i.e. it comprises positive and negative charges in the same molecule.

In one preferred embodiment of the invention the anionic counter ions are derived from mono- or polycarboxylic acids, i.e. they comprise at least one –COO^- group. In particular, suitable anionic counter ions are derived from aliphatic and/or aromatic carboxylic acids, in particular mono- or dicarboxylic acids comprising 1 to 20, preferably 1 to 12 carbon atoms. Examples of counter ions comprise the anions of formic acid, acetic acid, phthalic acid, isophthalic acid, or of C_2- to C_6-dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid or adipic acid. Examples of preferred counter ion comprise formate and acetate, in particular acetate.

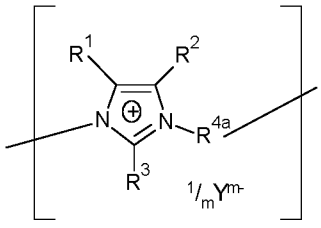
Further examples of suitable counter ions are disclosed in detail in US 2011/0263810 A1 paragraphs [0052] to [0074].

Surprisingly, it has been found that the molecular weight of the water-soluble cationic polymers to be used in the method according to the present invention has a pronounced effect on the performance of the polymers for the inhibition of the swelling of clay in subterranean formations.

Accordingly, the cationic polymers to be used in present invention have a weight average molecular weight M_w of at most 30,000 g/mol, in particular 1,000 g/mol to 30,000 g/mol, preferably 1,500 g/mol to 20,000 g/mol, , most preferably 2,000 g/mol to 15,000 g/mol.

Preferred cationic polymers

In a preferred embodiment the cationic polymer to be used according to the invention comprises at least 50 mol % of repeating units (Ia) with respect to all repeating units, preferably at least 80 mol % , more preferably at least 90 mol %, in particular at least 95 mol % and more preferably the polymer comprises only repeating units (Ia).

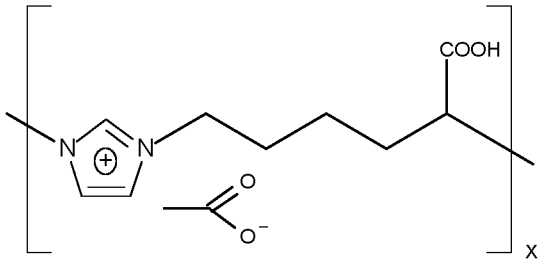


(Ia)

In the preferred embodiment R^1, R^2 and R^3 preferably are H. Furthermore, the groups R^{4a} are independently from each other C_2 to C_{20} alkylene groups, preferably C_4 to C_{12} alkylene groups, more preferably C_4 to C_8 alkylene groups which groups R^{4a} may be substituted by at least one carboxyl group. The groups R^{4a} which are substituted by at least one carboxyl group, in particular in 2-position, are preferred. Examples of such groups comprise 1,4-butylene, 1,5-pentylene, 1,6-hexylene, 1,7-heptylene and 1,8-octylene groups. Most

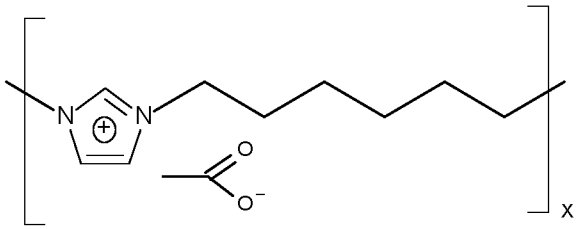
preferably R^{4a} is 1,6-hexylene. The anions Y^{m-} preferably are anions of carboxylic acids, in particular formate or acetate and most preferred acetate.

A preferred polymer is derived from formaldehyde, glyoxal and lysine in the presence of acetic acid according to method (II) and may be represented by the following formula



wherein x is 10 to 70, preferably 15 to 60.

Another polymer may be derived from formaldehyde, glyoxal and 1,6-hexanediamine in the presence of acetic acid according to method (II) and may be represented by the following formula.



wherein x is 10 to 70, preferably 15 to 60.

Synthesis of the cationic polymers

The cationic polymers comprising imidazolium groups described above may be synthesized by any method. Suitable methods are known to the skilled artisan.

Method (I)

In one embodiment the polymers may be synthesized by the process disclosed in WO 2010/072571. The method is a two-step process: In the first step an alkylene bridged bisimidazole Im-$(CH_2)_o$-Im (Im= imidazole) is synthesized which in the second step is reacted with an alkylene dibromide such as 1,3-dibromopropane thus yielding a polymeric imidazolium compound.

Method (II)

Starting materials for method (II)

In a preferred embodiment of the invention, the polymeric imidazolium salts are available by a process wherein at least an α-dicarbonyl compound, an aldehyde, at least one amino compound having 2 to 4 primary amino groups, and a protic acid are reacted with one another. Such a process has been described for instance in US 2011/0263810 A1.

The reaction is a polycondensation. In a polycondensation, polymerization occurs with elimination of a low molecular weight compound such as water or alcohol.

In the present case, water is eliminated in case of carbonyl groups. To the extent the carbonyl groups have the form of a ketal or hemiketal, acetal or hemiacetal group, an alcohol is eliminated instead of water.

The α-dicarbonyl compound is preferably a compound of the formula R^1-CO-CO-R^2 (III) wherein R^1 and R^2 have the meaning a defined above. The compound (III) is particularly preferably glyoxal, i.e. both R^1 and R^2 are hydrogen.

The carbonyl groups of the α -dicarbonyl compound may also be present as ketal or hemiketal, preferably as hemiketal or ketal of a lower alcohol, e.g. a C_1- to C_{10}-alkanol. In this case, the alcohol is eliminated in the later condensation reaction. The carbonyl groups of the α-dicarbonyl compound are preferably not present as hemiketal or ketal.

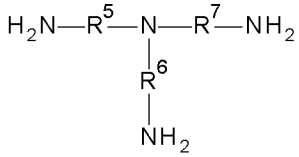
The aldehyde is in particular an aldehyde of the formula R^3-CHO (IV), wherein R^3 has the meaning as defined above. Particular preference is given to formaldehyde, i.e. R^3 = H; the formaldehyde can also be used in the form of compounds which liberate formaldehyde, e.g. paraformaldehyde or trioxane.

The aldehyde group of the aldehyde may also be present as hemiacetal or acetal, preferably as hemiacetal or acetal of a lower alcohol, e.g. a C_1- to C_{10}-alkanol. In this case, the alcohol is eliminated in the later condensation reaction. The aldehyde group is preferably not present as hemiacetal or acetal.

The amino compound is a compound having 2 to 4 primary amino groups. An amino compound with 2 primary amino groups is used for preparing the units of formula (Ia) whereas an amino compound with 3 or 4 primary amino groups leads to units of formula (Ib) or (Ic), respectively. The amino compound can be represented by the general formula $R^4(-NH_2)_n$ (V), wherein n is 2, 3, or 4 and R^4 is a 2- to 4-valent organic moiety which has the meaning as defined above. R^4 may be selected from the group of R^{4a}, R^{4b}, and R^{4c}, i.e. the amino compounds may be selected from diamines H_2N-R^{4a}-NH_2, triamines $R^{4b}(-NH_2)_3$, and tetraamines $R^{4c}(-NH_2)_4$.

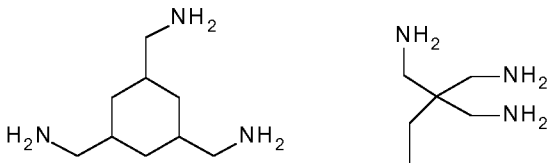
Diamines H_2N-R^{4a}-NH_2 which may be mentioned are, in particular, C_2 to C_{20}-alkylenediamines, preferably C_4- to C_{12} diamines such as 1,4-butylenediamine or 1,6-hexylenediamine.

Examples of possible triamines $R^{4b}(-NH_2)_3$ comprise aliphatic compounds of the formula (VI)

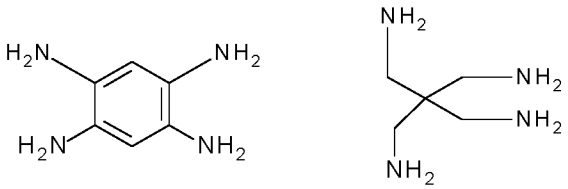


wherein R^5, R^6 and R^7 each, independently of one another have the meaning as defined above. An example which may be mentioned is triaminoethylamine (R^5=R^6=R^7= ethylene).

Further examples of possible triamines $R^{4b}(-NH_2)_3$ comprise amines of the following formulas:



Examples of possible tetraamines $R^{4c}(-NH_2)_4$ comprise



For preparing polymers comprising also units of formula (Ib) and/or (Ic) mixtures of amino compounds are used in the process of the invention. The use of such mixtures makes it possible to set desired properties such as glass transition temperature, elasticity, hardness or solubility in water in a targeted way.

It is of course possible to use further compounds, e.g. in order to introduce specific end groups or additional functional groups into the polymer to set defined properties. For instance, it may be possible to use compounds having only one primary amino group in order to influence the molecular weight of the polymeric imidazolium compounds or it may be possible to use compounds having more than 4 amino groups, however it is preferred to use no other amines than those of the general formula (V).

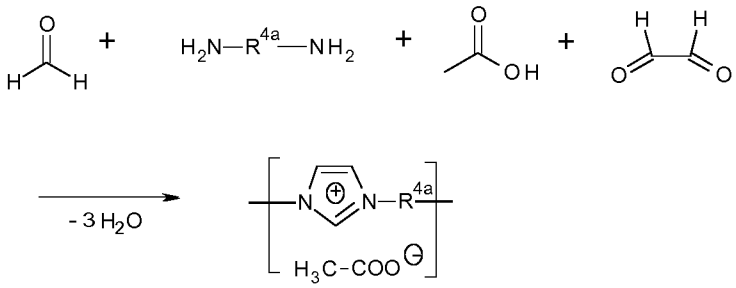
The protic acid which is used in method (II) may be represented by the formula $Y^{m-}(H^+)_m$, where Y^{m-} has the meaning as defined above. The anion Y^{m-} of the protic acid forms the counterion to the imidazolium groups of the cationic polymer.

The anion of a protic acid is preferably the anion of a protic acid having a pK_a of at least 1, in particular at least 2 and in a very particularly preferred embodiment at least 4. The pK_a is the negative logarithm to the base 10 of the acid constant, K_a. The pK_a is for this purpose measured at 25°C, 1 bar, either in water or dimethyl sulfoxide as solvent; it is therefore sufficient, according to the invention, for an anion to have the corresponding pK_a either in water or in dimethyl sulfoxide. Dimethyl sulfoxide is used particularly when the anion is not readily soluble in water. Information on the two solvents may be found in standard reference works.

Suitable anions / acids have already been disclosed above. Preferred protic acids are carboxylic acids, sulfonic acids, phosphoric acids or phosphonic acids. Further examples of suitable acids are disclosed in detail in US 2011/0263810 A1 paragraphs [0052] to [0074].

In one preferred embodiment of the preferred method for making the polymers the acids are mono- or polycarboxylic acids. In particular, suitable acids comprise aliphatic and/or aromatic carboxylic acids, in particular mono- or dicarboxylic acids comprising 1 to 20, preferably 1 to 12 carbon atoms, such as formic acid, acetic acid, phthalic acid, isophthalic acid, C_2- to C_6-dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid or adipic acid. Most preferred are formic acid and acetic acid, in particular acetic acid.

The reaction according to method (II) proceeds in principle according to the following reaction equation.



Here, 1 mol of aldehyde, 1 mol of a diamine, 1 mol of the protic acid and 1 mol of the α-dicarbonyl compound are used. In the polymer obtained, the imidazolium groups are joined to one another by the diamine.

High molecular weights in polycondensations should be achieved when the compounds are used in equimolar amounts.

Surprisingly, it has been found however, that the formation of polymers having high molecular weight is improved with a molar ratio of the α-dicarbonyl compound to the oligoamine of greater than 1; hence a molar excess of the α-dicarbonyl compound is used.

In a preferred embodiment the molar ratio the of α-dicarbonyl compound to the oligoamine is from 1.001 : 1 to 2 : 1, more preferred is a ratio of 1.01 :1 to 1.01 : 1.5; particularly preferred is a ratio of the of α-dicarbonyl compound to the oligoamine of 1.01 : 1 to 1.01 :1.2.

The aldehyde may be used in molar excess as well, so that the molar ratio of the aldehyde to the oligoamine is greater than 1. Preferably, aldehyde and oligoamine are used in equimolar amounts.

The reaction of the starting compounds is preferably carried out in water, a water-miscible solvent or mixtures thereof or, preferably, in a mixture of water and a water-immiscible solvent.

Water-miscible solvents are, in particular, protic solvents, preferably aliphatic alcohols or ethers having not more than 4 carbon atoms, e.g. methanol, ethanol, methyl ethyl ether, tetrahydrofuran. Suitable protic solvents are miscible with water in any ratio (at 1 bar, 21°C).

Suitable water-immiscible solvents are hydrocarbons, such as hexane or toluene.

During the reaction the pH value is preferably 1 to 7, most preferably 3 to 5. The pH value may be kept or adjusted by any suitable manner, for example by adding acids or suitable buffer systems. In a preferred embodiment an excess of the protic acid which is used as starting material may be used to adjust the pH value.

In a preferred embodiment the molar ratio of the protic acid to the oligoamine may be from 1.05 : 1 to 10 : 1, in particular from 1.2 to 5, respectively 1.5 to 5.

The starting components can be combined in any order.

The reaction of the starting components can be carried out at, for example, pressures of from 0.1 to 10 bar, in particular atmospheric pressure.

The reaction temperature may be below 100°C, for example from 0°C to 100°C, in particular from 20°C to 100°C. The reaction is exothermic and cooling may be required. In one embodiment the reaction may be started at temperatures below 100°C, in particular below 50°C, particularly preferably below 40°C, respectively 30°C. In order to avoid freezing the starting temperature should preferably be not lower than 0°C, in particular not be lower than 3 °C (at normal pressure). After starting the reaction the temperature increases due to the exothermic reaction. The temperature should rise to temperatures of at least 80°C, for

examples 80°C to 100°C, preferably at least 90°C, preferably 90°C to 100°C. If the heat generated by the exothermic reaction is not enough to achieve the temperatures it may be necessary to heat reaction mixture.

The reaction can be carried out batchwise, semicontinuously or continuously. In the semicontinuous mode of operation, it is possible, for example, for at least one starting compound to be initially charged and the other starting components to be metered in.

In the continuous mode of operation, the starting components are combined continuously and the product mixture is discharged continuously. The starting components can be fed in either individually or as a mixture of all or part of the starting components. In a particular embodiment, the amine and the acid are mixed beforehand and fed in as one stream, while the other components can be fed in either individually or likewise as a mixture (2nd stream).

In a further particular embodiment of a continuous process all starting components comprising carbonyl groups (i.e. the α-dicarbonyl compound, the aldehyde and the protic acid of the anion X (if the latter is a carboxylate) are mixed beforehand and fed in together as a stream; the remaining amino compound is then fed in separately.

The continuous preparation can be carried out in any reaction vessels, i.e. in a stirred vessel. It is preferably carried out in a cascade of stirred vessels, e.g. from 2 to 4 stirred vessels, or in a tube reactor.

In a preferred embodiment of a batchwise process the protic acid is placed in the reactor first and the oligoamine, aldehyde and α-dicarbonyl compound are fed to the protic acid in a rate that the temperature of the reaction mixture is kept below 40 °C, respectively 30°C. With such prodecure the formation of any precipitates during the reaction is essentially avoided.

After the polycondensation reaction has been carried out, the polymeric compounds obtained can precipitate from the solution or remain in solution. Preferably solutions of the polymeric ionic imidazolium compounds are obtained.

The polymeric compounds can also be separated off from the solutions by customary methods. In the simplest case, the solvent, e.g. water, can be removed by distillation or by spray drying.

Method of inhibiting the swelling of clay

For the method of inhibiting the swelling of clay in subterranean formations according to the present invention a carrier fluid comprising at least one of the cationic polymers of the invention as described above is provided and the carrier fluid is introduced into the subterranean formation.

The cationic polymers comprising imidazolium groups reduce, prevent or eliminate completely formation damage to the subterranean formation due to clay swelling and/or migration and/or disintegration of the clay due to exposure of connate waters or introduced treatment fluids.

The method of inhibiting the swelling of clay in subterranean formations according to the present invention yields a permanent inhibition. Thus, the cationic polymers are suitable as clay stabilizers or shale inhibitors, in particular in oil drillings. The inhibiting effect can be determined by the Shale Particle Disintegration Test as described in the examples section. A decrease of the FANN® values after ageing means inhibition of the swelling of clay. The term “permanent” means that the inhibiting effect not only occurs as long as the clay is in contact with the carrier fluid comprising the inhibiting polymer but at least some inhibiting effect remains at least for some time after the clay is no longer in contact with the carrier fluid comprising the inhibiting polymer but with aqueous fluids which do not comprise an inhibitor such as formation water and/or other injected fluids.

The carrier fluid may be an aqueous fluid. An aqueous fluid may comprise also organic solvents miscible with water. Usually, the amount of water is at least 50 % by weight relating to the total amount of all solvents used, preferably at least 70 % by weight, more preferably at least 90 % by weight. In one embodiment of the invention only water is used. The water used may be fresh water but also water comprising salts such as brine, sea water or formation water may be used.

The concentration of the cationic polymers comprising imidazolium groups used in the method according to the present invention may be selected by the skilled artisan according to his/her needs. Usually, the concentration of the polymeric imidazolium salts used according to the present invention is from 0,001% to 1 % by weight, preferably from 0,005 % to 0,5 % by weight and most preferably 0,01 % to 0,1 % by weight, based on the total weight of the formulation. When used as shale inhibitor, in particular in drilling processes, the polymeric imidazolium salts are in general used in an amount of 0.1 to 5 % by weight, preferably 0.5 to 1% by weight, based on the total weight of the formulation. When used for hydraulic fracturing, the polymeric imidazolium salts are in general used in an amount of 0.01 to 1 % by weight, preferably 0.02 to 0.5 % by weight, based on the total weight of the formulation.

Of course, also a mixture of two or more different cationic polymers comprising imidazolium groups may be used. Furthermore, the cationic polymers comprising imidazolium groups may be combined with chemically different clay inhibitors.

Besides the polymeric imidazolium salts the carrier fluid may of course comprise further components. The kind and amount of further components depends on the specific use of the fluid.

Examples of suitable carrier fluids comprise drilling fluids, completion fluids, stimulation fluids such as fracturing fluids, including but not limited to acidic fracturing fluids, alkaline fracturing fluids and foamed fracturing fluids, matrix acidizing fluids, production/remediation fluids, fluids for enhanced oil recovery (EOR), gravel packs, frac and pack fluids, and wellbore clean up fluids. Components contained in such fluids are known to the skilled artisan. Drilling fluids are the preferred carrier fluids.

In another embodiment of the invention, the carrier fluid comprising at least one cationic polymer comprising imidazolium salts may be used for pre-flushing the formation, i.e. the formation is first treated with an aqueous fluid comprising the clay inhibitor followed by treatment with the desired treatment fluid, such as the fluids mentioned previously. Due to the permanent clay stabilization effect of the polymeric imidazolium salts used according to the present invention, such treatment fluids need not to contain clay stabilizers although this is possible.

Any kind of clay may be treated with the polymeric imidazolium salts according to the present invention. Examples of clays include montmorillonite, saponite, nontronite, hectorite, and sauconite, kaolinite, nacrite, dickite, halloysite, hydrobiotite, glauconite, illite, bramallite, chlorite or chamosite. Besides clays the formation may of course comprise other minerals.

Surprisingly, it has been found that the cationic polymers comprising imidazolium groups lower the freezing point of aqueous formulations which is an additional benefit if aqueous formulations are used at low temperatures, e.g. in artic regions.

In a preferred embodiment of the invention the cationic polymers comprising imidazolium salts may be used for stimulation applications, including but not limited to fracturing and acidizing.

For hydraulic fracturing a fluid comprising at least a carrier fluid, preferably an aqueous carrier fluid, a thickener, a proppant and at least one cationic polymer comprising imidazolium groups as described above is used which is injected into the formation at a pressure sufficient to fracture the formation. The thickener may comprise thickening polymers such as guar or cellulose type polymers or thickening surfactants, e.g. viscoelastic surfactants.

For acidizing a fluid comprising at least a carrier fluid, preferably an aqueous carrier fluid, an acid and at least one cationic polymer comprising imidazolium groups as described above is used which is injected into the formation. Examples of suitable acids comprise HF and/or HCl

and methane sulfonic acid. In matrix acidizing operations the carrier fluid is injected at a pressure not sufficient to fracture the formation, i.e. the permeability of the formation is only increased by impact of the acid whereas in fracture acidizing operations the carrier fluid is injected at a pressure sufficient to fracture the formation.

The following examples are intended to illustrate the invention in detail:

The molecular weight of the obtained polymers was determined by gel permeation chromatography (GPC) (standard: Pullulan; effluent: water).

Tested samples:

For the tests the following polyimidazolium salts were synthesized:

Sample 1:
Polyimidazolium salt based on lysine (H_2N-$(CH_2)_4$-CH(-NH_2)(-COOH))

A flask was charged with a mixture of 120.10 g acetic acid (2 moles) and 100 g water. 584.80 g of lysine (2 moles; 50 wt.-% aqueous solution) were added dropwise with stirring within 45 min. to the mixture. Thereafter, a mixture of 40.00 g of glyoxal (2 moles; 40 wt.-% aqueous solution) and 122.60 g of formaldehyde (2 moles; 49 wt.-% aqueous solution) was added dropwise with stirring within 20 min. During the additions the temperature was kept in the range from 17 to 21 °C. Stirring was then continued at a bath temperature of 105 °C for 40 min. During the entire process a stream of carbon dioxide was passed through the reaction mixture. A polymer solution with a solid content of 35.3 wt.-% was obtained.

GPC: M_n 3570 g/mol; M_w 6180 g/mol.

Sample 2:
Polyimidazolium salt based on lysine (H_2N-$(CH_2)_4$-CH(-NH_2)(-COOH))

2 Mole acetic acid dissolved in a mixture of 50 g water and 350 g toluene were placed in a flask. A mixture of 1.00 mole formaldehyde (49% aq. Solution) and 1,00 mole glyoxal (40% aq. Solution) was added via a dropping funnel to the solution. In parallel, 1,09 mole of Lysine·HCl was added as a solid. During addition of the monomers the reaction mixture is held at room temperature by ice bath cooling. After completion of the addition the reaction mixture is heated to 100 °C for 1 hour. The organic layer is separated and an aqueous solution of the polymeric, ionic imidazolium compound is obtained.

GPC: Mn = 2,200 g/mol; Mw = 4,800 g/mol.

Sample 3:

Polyimidazolium salt based on lysine (H_2N-$(CH_2)_4$-CH(-NH_2)(-COOH))

Sample 3 was prepared as described for sample 2 but using 1.03 mole lysine · HCl.

GPC: Mn = 2,900 g/mol; Mw = 7,300 g/mol.

Sample 4:
Polyimidazolium salt based on lysine (H_2N-$(CH_2)_4$-CH(-NH_2)(-COOH))

Sample 4 was prepared as described for sample 2 but using 1.0 mole lysine · HCl.

GPC: Mn = 5,900 g/mol; Mw = 13,300 g/mol.

Sample 5:
Polyimidazolium acetate based on 1,4-tetramethylenediamine , M_w 10500 g/mol

Sample 5 was synthesized according to the following procedure:

2 Moles acetic acid dissolved in 100 g water were placed in a flask. A mixture of 1.00 mole formaldehyde (49% aq. Solution) and 1,00 mole glyoxal (40% aq. Solution) was added via a dropping funnel to the solution. In parallel, 0,66 mole of 1,4-tetramethylenediamine and 0,66 mole of dodecylamine were added to the solution via a separate dropping funnel. During addition of the monomers the reaction mixture is held at room temperature by ice bath cooling. After completion of the addition the reaction mixture is heated to 100 °C for 1 hour. An aqueous solution of the polymeric, ionic imidazolium compound is obtained.

M_W: 10500 g/mol, M_n 4400 g/mol)

Sample 6:
Polyimidazolium acetate based on 1,12-dodecamethylenediamine , M_w 21500 g/mol

Sample 6 was synthesized by repeating the procedure of sample 5 but using 0,9 mol 1,12-dodecylmethylenediamine formaldehyde and 0,2 mol dodecylmethyleneamine.
M_W: 21500 g/mol, M_n 14000 g/mol.

The samples were subjected to the following tests:

Shale Particle Disintegration Test

This test is used to screen the effectiveness of shale inhibitors to maintain the integrity of cuttings and minimize the interaction of fluids with the shale sections during the drilling and completion operations. The test is described in “Shale Particle Disintegration Test by Hot Rolling”, Section 22 in: API Recommended Practices 13I: Laboratory Testing of Drilling

Fluids, 7th ed. and ISO 10416:2002; American Petroleum Institute (February 2004), 73-76. It was carried out as follows:

350 ml of tap water were charged into a HB mixing beaker (Hamilton Beach type mixer with metal beakers). 2.5 g of sample 1 (5g of the 50% solution) were added and stirred for 20 minutes for dissolution. 10.5 g NaCl (3% based on 350 g total weight) were added and the beaker was fastened at the HB mixer. 30 ppb (pounds per barrel; 8.5%) Cebogel (cylindrical bentonite rods) were added with stirring and mixed at the HB mixer for 10 minutes at low speed. Shortly before the end of mixing the pH was determined. FANN® rheology and gel strength were determined from the mixture. The washings were placed into aging cells and charged with 200 psi (13.79 bar) of nitrogen. The cells were flushed with nitrogen and then pressurized again. The washings were subjected to aging for 16 h at 200°F (93.3 °C) in a roller oven. The cells were cooled for 30 min. at the air (with open door of the roller oven) and thereafter for 30 min. in a water bath. After venting the muds were given into a HB mixing beaker and stirred for 5 min. at low speed. Thereafter, pH, FANN® rheology and gel strength were determined.

Cutting Hardness Test (Bulk Hardness Test)

The bulk hardness test is designed to evaluate the hardness of shale after exposure to fluids. The bulk hardness test and a bulk hardness tester are described by Patel et al. in AADE 01-NC-HO-55, paper presented at the AADE 2001 National Drilling Conference, “Drilling Technology – The Next 100 years” and Stephens et al. in AADE National Drilling Technical Conference 2009

The test was carried out as follows:

Bentonite cuttings Bentone® GWB 2-5 mm were obtained from Tolsa UK Ltd., Middlesbrough.

The test was carried out with mud of the following composition:

Tap water (mL)	323
NaCl (g)	73.2
NaOH (g)	1.0
Cebogel (g)	10
Polydrill (g)	2.5
Shale Inhibitor (g)	7.1

323 ml of tap water was charged into a HB mixing beaker. 73.2 g NaCl and 1.0 g sodium hydroxide were added and stirred at the HB mixer for 5 min. at low speed. 10 g of Cebogel

(cylindrical bentonite rods) were added and stirred at the HB mixer for 5 minutes at low speed. 2.5 g of Polydrill® (sulfonated, anionic synthetic polymer) were added with stirring and stirring was continued for 10 min. 7.1 g of sample 1 (2.5 g actives) were added and stirred for 20 minutes for dissolution. FANN® 35 rheology and pH of the solution were determined. 350 ml of the mud were placed into an aging cell. In addition, 50 g bentonite pieces (GWB GRAN, 2.5 mm of TOLSA UK LTD.) were added to the mud shortly before aging. The cell was charged with 150 psi (10.34 bar) of nitrogen. The pressure was released and the cell was flushed with nitrogen and then pressurized again and subjected to aging for 16 h at 150°F (65.6 °C) in a roller oven. The cell was cooled for 30 min. in the roller oven with open door and thereafter for 30 min. in a water bath. After venting the mud was given over a 500 µm sieve and rinsed with at least 250 ml brine until the bentonite pieces were free of mud. The pieces were placed into a cutting hardness tester. Using a torque wrench the pieces were extruded through a perforated plate, the cuttings were collected and the continuous torque was measured.

Sieve Test (Dispersion Test)

The test is described by Stephens et al. in AADE 2009 NTCE-11-04 (National Technical Conference & Exhibition, New Orleans, Louisiana and was carried out as follows: a 10 wt.-% bentonite suspension was stirred and allowed to swell in tap water. A 15 ppb KCl solution (washing solution) was prepared by dissolving 15 KCl in 350 ml tap water. North Sea water was prepared by mixing the following components:

5000 g	distilled water
1.13 g	$NaHCO_3$
13.60 g	$CaCl_2x6H_2O$
28.34 g	$MgCl_2x6H_2O$
39.7 g	$MgSO_4x7H_2O$
158.72 g	NaCl

Cuttings: Bentonite cuttings Bentone® GWB 2-5 mm.

305 g North Sea water were charged into a HBM cup followed by 50 g of a 10 wt.-% bentonite suspension. The mixture was stirred for 5 min. at low speed. Thereafter, 14.2 g of sample 1 (5 g of actives) were added to the mixture and the resulting mixture was stirred for 5 min. in addition, 1 drop of defoamer Degressal SD 21 (obtainable from BASF SE) and 2.5 g of IDCAP D (encapsulator; low molecular weight acrylic acid copolymer) were added to give a drilling fluid.

The drilling fluid was divided into 2 parts and each part was charged into a plastic bottle. 25 g of the cuttings were added to each bottle. The bottles were vigorously shaken and subjected to aging in a roller oven at 60 °C for 16h. The content of each bottle was poured onto a sieve, washed with the washing solution until the filtrate was clear. The KCl residues were removed by washing with water. The clean cuttings were dried at 110 °C until the weight was constant (at least 2h) and weighed.

The results are given in the following tables 1 to 3:

Shale Particle Disintegration Test

Table 1:

Sample	NaCl Amount [%]	Before Ageing FANN 35 reading [lb/100ft²]						PV [cP]	YP [lb/100ft²]	Gel strength 10``/10` [lb/100ft²]
		600	300	200	100	6	3			
Blind sample	0.0	50	36	31	25	18	17	14	22	27/53
	3.0	9	6	5	3	2	2	3	3	3/6
Ultrahib	0.0	112	94	90	83	72	49	18	76	44/37
	3.0	4	2	1	1	0	0	2	0	1/2
Sample 1 Solids = 35.3%	0.0	52	46	45	44	44	33	6	40	27/32
	3.0	8	5	4	3	2	1	3	2	3/4

Ultrahib: Shale inhibitor of M-I Swaco (polyamine on ethylene glycol basis)

Table 2

Sample	NaCl Amount [%]	After Ageing FANN 35 reading [lb/100ft²]						PV [cP]	YP [lb/100ft²]	Gel strength 10``/10` [lb/100ft²]
		600	300	200	100	6	3			
Blind sample	0.0	64	44	32	28	17	17	20	24	27/46
	3.0	12	8	7	5	3	3	4	4	4/7
Ultrahib	0.0	16	9	7	4	1	1	7	2	1/1
	3.0	4	2	1	0	0	0	2	0	1/1
Sample 1 Solids = 35.3%	0.0	19	13	10	7	4	4	6	7	6/13
	3.0	8	5	4	3	1	1	3	2	2/4

A reduction of the FANN® values after ageing by at least 10% is considered as inhibiting effect.

Cutting Hardness Test

Table 3:

Polymer		Blind value	Ultrahib	Sample 1	Sample 5
Amount [g]			2.5	7.1	4.0
Rheology FANN	600	6	5	4	4
	300	3	3	2	2
	200	2	2	1	1
	100	1	1	1	0
	6	1	1	0	0
	3	1	1	0	0
PV [cP]		3	2	2	2
YP [lb/100ft²]		0	1	0	0
Force		10	40	15	20
Cuttings		yes	yes	yes	Yes
Pellet		no	1mm	no	No
Remark:		Cuttings: soft, crumbly	Cuttings: soft, crumbly	Cuttings: medium hard	Cuttings: soft

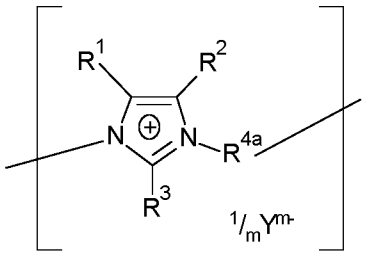
Sieve-Test:

Table 4:

Shale Inhibitor Name/ Amount	Encapsulator Name/ Amount	Water Consumption of Cuttings %	Average Water Consumption wet %	Residue %	Average Residue %
Blind value Sea water		33,32	28,62	67.7	66,9
		23,92		66.0	
Ultrahib 10.0	**IDCAP D 2.5g**	46.56	53.14	91.6	92.1
		59.72		92.5	
Sample 1 10.0	**IDCAP D 2.5g**	41.84	45.76	87.2	86.9
		49.68		86.6	
		38.96		85.7	
		45.40		86.4	
Sample 5 8.1g	**IDCAP D 2.5g**	39.12	34.68	83.5	83.7
		30.24		83.8	

Claims

1. A method of inhibiting the swelling of clay in subterranean formations comprising the step of introducing an aqueous carrier fluid into the formation wherein the carrier fluid comprises at least one clay stabilizer which is a cationic polymer comprising repeating units (Ia) of the formula



(Ia)

wherein

R^1, R^2, and R^3 are each, independently of one another, H or a saturated or unsaturated, branched or unbranched, aliphatic and/or aromatic hydrocarbon moiety having from 1 to 20 carbon atoms which optionally may be substituted with functional groups,

R^{4a}, R^{4b}, R^{4c} are each, independently from one another, organic groups comprising 2 to 50 carbon atoms, wherein the organic groups R^{4a}, R^{4b}, and R^{4c} may optionally comprise functional groups and/or non-neighboring carbon atoms may be substituted by heteroatoms,

Y^{m-} are each, independently of one another, anionic counter ions, wherein m is an integer from 1 to 4,

and wherein the cationic polymer has a weight average molecular weight M_w of about 1,000 g/mol to about 30,000 g/mol.

2. The method according to claim 1, wherein the weight average molecular weight M_w is from about 1,500 g/mol to about 20,000 g/mol, in particular from about 2,000 g/mol to about 15,000 g/mol.

3. The method according to claim 1 or 2, wherein R^{4a} comprises 2 to 20 carbon atoms.

4. The method according to any of claims 1 to 3, wherein R^{4a} comprises at least one group selected from the group of carboxylic acid groups, ether groups, secondary amino groups or tertiary amino groups.

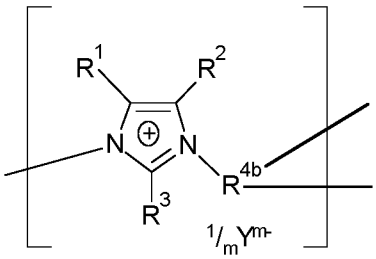
5. The method according to any of claims 1 to 4, wherein $R^{4a}$is an aliphatic group which is optionally substituted with at least one carboxylic acid group.

6. The method according to any of claims 1 to 5, wherein R^{4a} is a C_2 to C_{20} alkylene group which is optionally substituted with at least one carboxylic acid group, in particular a C_4 to C_{12} alkylene group which is optionally substituted with at least one carboxylic acid group.

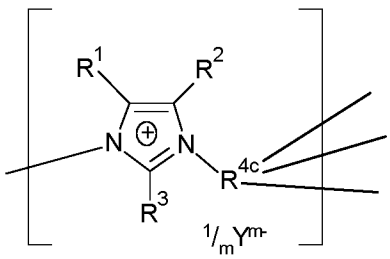
7. The method according to claim 8, wherein R^{4a} is a C_4 to C_{12} alkylene group or a C_5 alkylene group which is substituted with a carboxylic acid group.

8. The method according to any of claims 1 to 7, wherein R^1, R^2, and R^3 are H.

9. The method according to any of claims 1 to 8, wherein the cationic polymer comprises in addition repeating units of the formula (Ib) and/or (Ic)



(Ib)



(Ic)

,

wherein R^1, R^2, and R^3 are as defined in claims 1 or 8, m and Y is as defined in claim 1 and R^{4b}, and R^{4c} have the same meanings as R^{4a} as given in any one of claims 1, or 3 to 7.

10. The method according to any of claims 1 to 5, wherein the cationic polymer comprises only repeating units (Ia).

11. The method according to claim 9, wherein the amount of repeating units (Ia) is at least 80 mol %, preferably at least 90 mol %, relating to the total amount of all repeating units.

12. The method according to claim 9 or 11, wherein the amount of repeating units (Ib) and/or (Ic) is up to 20 mol %, wherein the total amount of units(Ib) or (Ic) is not more than 20 mol %.

13. The method according to claim 9 or 11, wherein the amount of repeating units (Ib) and/or (Ic) is up to 10 mol %, wherein the total amount of units(Ib) or (Ic) is not more than 10 mol %.

14. The method according to claim 9 or 11, wherein the amount of repeating units (Ib) or (Ic) is up to 5 mol %, wherein the total amount of units(Ib) or (Ic) is not more than 5 mol %.

15. Method according to any of claims 1 to 14, wherein Y^{m-} is an anion of a mono- or polycarboxylic acid.

16. Method according to claim 15, wherein Y^{m-} is an acetate ion.

17. Method according to any of claims 1 to 16, wherein the concentration of the cationic polymers in the carrier fluid is from 0,001% to 1 % by weight relating to the amount of all components of the carrier fluid.

18. Method according to any one of claims 1 to 17, wherein the carrier fluid is selected from the group of drilling fluids, completion fluids, stimulation fluids such as fracturing fluids, including but not limited to acidic fracturing fluids, alkaline fracturing fluids and foamed fracturing fluids, matrix acidizing fluids, production/remediation fluids, fluids for enhanced oil recovery (EOR), gravel packs, frac and pack fluids, and wellbore clean up fluids.

19. Method according to any of claims 1 to 18, wherein the carrier fluid is a pre-flush fluid and the treatment with the pre-flush fluid is followed by the treatment of the formation with a treatment fluid.

20. Method according to any of claims 1 to 18, wherein the carrier fluid is a hydraulic fracturing fluid comprising, in addition, at least a thickener and a proppant and the fluid

is injected into the formation at a pressure sufficient to fracture the formation.

21. The use of a polymer as defined in any one of claims 1 to 16 for inhibiting the swelling of clay in subterranean formations.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/079972

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/035 C09K8/52 C09K8/588 C09K8/60 C09K8/62
C09K8/70 C09K8/72 C09K8/88 E21B43/04 C09K8/68
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 E21B

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.
X	LIU XIANGJUN ET AL: "Synthesis and evaluation of novel water-soluble copolymers based on acrylamide and modular[beta]-cyclodex", CARBOHYDRATE POLYMERS, APPLIED SCIENCE PUBLISHERS, LTD. BARKING, GB, vol. 96, no. 1, 22 March 2013 (2013-03-22) , pages 47-56, XP028544274, ISSN: 0144-8617, DOI: 10.1016/J.CARBPOL.2013.03.053 page 53, paragraphs 3.7,3.8 - page 54; figure 1	1-21
A	US 2008/045420 A1 (KARAGIANNI KATERINA [FR] ET AL) 21 February 2008 (2008-02-21) paragraphs [0074], [0121], [0171] - [0174]; claims 42,47,61	1-21

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 February 2016	03/03/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Redecker, Michael

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/079972

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 152 906 A (AFTEN CARL W [US] ET AL) 6 October 1992 (1992-10-06) column 1, lines 10-15; claims 1,12; example 1 column 4, line 62 - column 6, line 8 -----	1-21
A	US 2010/256020 A1 (ASTON MARK [GB] ET AL) 7 October 2010 (2010-10-07) paragraph [0018]; claims 1,6; examples 1,9-11 -----	1-21

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/079972

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008045420 A1	21-02-2008	BR PI0417524 A	06-03-2007
		CN 1894292 A	10-01-2007
		EP 1694727 A2	30-08-2006
		FR 2863617 A1	17-06-2005
		RU 2333225 C2	10-09-2008
		US 2008045420 A1	21-02-2008
		WO 2005059860 A2	30-06-2005
US 5152906 A	06-10-1992	NONE	
US 2010256020 A1	07-10-2010	AT 530618 T	15-11-2011
		AU 2008332955 A1	11-06-2009
		AU 2008332957 A1	11-06-2009
		BR PI0820901 A2	23-06-2015
		BR PI0821064 A2	16-06-2015
		DK 2245108 T3	30-01-2012
		EA 201000955 A1	28-02-2011
		EA 201000956 A1	30-12-2010
		EP 2067835 A1	10-06-2009
		EP 2235135 A1	06-10-2010
		EP 2245108 A1	03-11-2010
		US 2010256019 A1	07-10-2010
		US 2010256020 A1	07-10-2010
		WO 2009071873 A1	11-06-2009
		WO 2009071875 A1	11-06-2009